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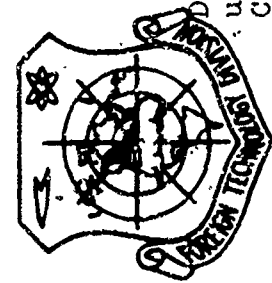
FOREIGN TECHNOLOGY DIVISION



THE METALLURGY OF TITANIUM

by

V. A. Garmata, B. S. Gulyanitskiy, et. al.



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## EDITED TRANSLATION

THE METALLURGY OF TITANIUM

By: V. A. Garmata, B. S. Gulyanitskiy, et. al.

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## FOREWORD

The directives of the Twenty-third Congress of the Communist Party of the Soviet Union in connection with the 1966-1970 Five-Year Plan for development of the USSR's national economy provide for an additional sharp increase in the production of new, progressive materials and their extensive introduction into the economy. These materials include titanium, which exhibits a number of valuable properties: high strength (referred to the density of the metal), outstanding chemical stability with respect to many corrosive media, and high heat resistance. It is to these properties that titanium and alloys based on it owe their extensive use in jet aviation, rocket engineering, weapons systems, and, most recently, in chemical engineering and radio electronics.

Industrial production of titanium was begun abroad in the late 1940's. Among the capitalist countries, the main producers of titanium are the USA, Great Britain, and Japan.

The titanium industry of the USA, which developed at an exceptionally rapid rate from 1951 through 1957 on the strength of large Air Force orders, was then stricken by a major crisis leading to a sharp drop in the production of the metal and a subsequent slower expansion rate of the industry. The American titanium industry is still not yet completely in control of such crisis effects, although production has been rising steadily over the last 2-3 years.

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Industrial production of titanium was set up in the Soviet Union in the early 1950's. Our titanium industry is an up-to-date branch of the socialist economy. Titanium output in the USSR is increasing steadily and at a rapid rate on a socialist economic planning basis.

The production of titanium and its broad-scale use in industry are now being held back by the relatively high cost of the metal. This is explained chiefly by the complexity of its technology and inadequate productivity of the equipment used in titanium production. Hence research toward new, more efficient methods of obtaining the metal are continuing in all countries that produce titanium, as indicated, for example, by the continuing publication of broad-scale scientific research papers and the frequent issuance of patents for new and improved production processes.

The present volume examines the technological processes and equipment used in the production of titanium sponge under industrial conditions. The principal subjects here are the preparation of the titanium-containing raw material for chlorination, the production and purification of titanium tetrachloride, and its reduction by magnesium and sodium.

At the same time, in view of the acknowledged shortcomings of the technology and equipment used at the present time and the intensive search for more effective solutions, the authors have also considered it necessary to include promising new methods that are still in the laboratory-research or pilot-plant stage.

Thus, it is difficult to overrate the prospects of such methods as the electrolytic production of titanium from titanium compounds, electrolytic and thermal refining of titanium, two-stage sodiothermic reduction of titanium, the various continuous processes for reduction of titanium tetrachloride and separation of the reduction products, etc.

The book devotes special attention to the quality of the intermediate products and the metal, which, together with the cost of the metal, is of prime importance for its practical use.

Utilization of titanium scrap, which still continues to accumulate in large quantities, must be an important factor in lowering the cost of titanium. A separate chapter is devoted to utilization of this scrap.

The chloride metallurgy on which titanium production technology is based opens broad new possibilities for the organization of large-scale industrial production not only of metallic titanium, but also of an important titanium compound - titanium dioxide, the production of which has been increasing steadily and rapidly in recent years. In this context, the book examines the production of titanium dioxide from the tetrachloride.

The chapters devoted to melting of titanium and powder metallurgy are included in the monograph to give a general notion of the complete chemicometallurgical cycle of titanium production. The authors do not pretend to have exhausted this material, and recommend that readers refer to the literature cited for detailed study of this question.

On 8 September 1961, the Committee on Standards, Measures, and Measuring Instruments in the USSR Council of Ministers approved a new state standard entitled "The International System of Units" (GOST 9887-61) for preferred use beginning 1 January 1963 in all branches of science and engineering.

Since all quantities are given in the old units in the present volume, we cite here the data needed to convert certain quantities from the older systems to the new SI system.

| Old and Out-of-System<br>Units    | SI Units   |
|-----------------------------------|--|
| 1 micron ( $\mu$ )                | 1 micrometer ( $\mu\text{m}$ ) = $10^{-6}$ m                           |
| 1 Angstrom $\text{\AA}$           | 0.1 nm = $10^{-10}$ m  |
| 1 liter (l)                       | $1.00028 \cdot 10^{-3}$ m <sup>3</sup>                                 |
| 1 ton (t)                         | 1000 kg  |
| 1 kilogram-force (kgf)            | 9.80665 N ( $\approx 9.81$ N)  |
| 1 dyne (dyn)                      | $10^{-5}$ N  |
| 1 kilogram-force-meter<br>(kgf·m) | 9.80665 N·m ( $\approx 9.81$ N·m) =<br>= 9.80665 J ( $\approx 9.81$ J) |
| 1 kilowatt-hour (kWhr)            | $3.6 \cdot 10^6$ J   |

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| Old and Out-of-System<br>Units  | SI Units                          |
|---------------------------------|-----------------------------------|
| 1 kilogram-calorie (kcal)       | 4186.8 J = 4.1868 kJ<br>(~4.2 kJ) |
| 1 kg·m/s                        | 9.80665 W (N·m/s)                 |
| 1 kgf/cm <sup>2</sup>           | 98066.5 N/m <sup>2</sup>          |
| 1 mm H <sub>2</sub> O           | 9.80665 N/m <sup>2</sup>          |
| 1 mm Hg                         | 133.322 N/m <sup>2</sup>          |
| 1 technical atmosphere<br>(atm) | 98066.5 N/m <sup>2</sup>          |

Author credits for the chapters in this monograph are: V.Yu. Kramnik, production of raw materials for chlorination; the late P.P. Khomyakov and G.V. Seryakov, production of titanium tetrachloride; V.A. Garmata, metallothermic methods of titanium production; B.S. Gulyanitskiy, Continuous titanium-production methods, the survey of the properties and fields of application of titanium, melting and recovering treated titanium wastes; A.B. Suchkov, electrolytic production and refining of titanium, the powder metallurgy of titanium; and Ya.M. Lipkes, refining of titanium and production of titanium dioxide.

"The Metallurgy of Titanium" is a first-edition monograph, and the authors will be grateful for reader comments, remarks, and criticism. The authors ask that all comments be addressed to the "Metallurgiya" publishing house.

UDC 669.295

Metallurgiya titana. Garreta, V.A., Gulyanitskiy, E.S., Kramnik, V.Yu., Lipkes, Ya.M., Seryakov, G.V., Suchkov, A.B., and Khomyakov, P.P. Izd-vo "Metallurgiya," 1967, 643 pages.

The book sets forth problems in the preparation of titanium-containing raw materials for chlorination. It examines the production of titanium tetrachloride, metalothermic methods of producing titanium, and the refining and remelting of the metal. Methods for electrolytic production and refinement of titanium, reclaiming titanium and titanium-alloy scrap, and production of pigment titanium dioxide from titanium tetrachloride are described. Attention is given to the properties of titanium and titanium-based alloys, and their fields of application are indicated.

The book is oriented to engineering, technical, and scientific workers, but may also be helpful to students specializing in titanium metallurgy at the institutes of technology.

With 150 Illustrations, 58 Tables, and Bibliographies with 965 source citations.

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PART I

TITANIUM, ITS PROPERTIES AND USES

## Chapter 1

### A BRIEF HISTORICAL OUTLINE OF TITANIUM PRODUCTION

In 1789, while studying the chemical composition of a magnetic sand from the village of Manaccan, the English scientist W. Gregor found a new earth, which he named manaccanitic earth. In 1795, M. Klaproth found a hitherto unknown metal in the mineral rutile and named it titanium; two years later, he himself established the identity between rutile and manaccanitic earth. In a study of metal-like crystals in blast-furnace slags, W. Wollaston concluded in 1822 that they were composed of practically pure titanium. In 1825, J. Berzelius prepared impure mechanical titanium by reducing potassium fluotitanate  $K_2TiF_6$  with potassium. Its properties differed from those of the titanium prepared by Wollaston, but this was explained by the noncrystalline structure of Berzelius' titanium. Not until 1849 did F. Wöhler demonstrate by burning blast-furnace crystals in a current of chlorine that Wollaston's "titanium" was in fact the compound  $Ti_5Cn_4$  [1].

In describing the titanium compounds in the 1906 edition of his "Osnovy khimii" [The Fundamentals of Chemistry], the last published before his death, D.I. Mendeleev had only a few words for the metal itself: a gray powder with a density of  $3.65 \text{ g/cm}^3$  [2].

In 1887, L. Nilson and O. used sodium to reduce titanium tetrachloride in a steel bomb. They obtained titanium

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with a purity of about 95% [3].

In 1910, M. Hunter prepared a relatively pure and ductile titanium (99.7-99.8% Ti), again by reducing titanium tetrachloride with sodium in a steel bomb. According to his observations, the reduction occurs instantaneously and explosively, and is accompanied by the development of high pressures [4]. In 1921, M. Billy published the results of experiments in which titanium tetrachloride was reduced with sodium hydride at pressures near atmospheric [5].

In 1925, van Arkel and de Boer, using a method that they had developed for thermal dissociation of titanium iodide, prepared small quantities of metal free of nonmetallic impurities from sodium-reduced titanium [6]. A series of studies of the physical and mechanical properties of highly pure titanium was carried out over the next fifteen years in Holland. It was found that metallic titanium could be a valuable structural material if it could be produced by an economical industrial method. However, as late as 1948, titanium was still being described as a brittle metal useful chiefly for alloying and dioxiding steels.

During the Second World War, the firm Degussa in Germany produced titanium by the sodiothermic method in agitator-equipped steel reactors. The titanium was of moderate purity, at about 98%. The chief impurities were oxygen and iron [7].

The bases of the magnesiothermic method of producing titanium that is now in widespread use were published by W. Kroll in 1940 [8]; the work to bring the Kroll process up to full industrial scale was begun by the US Bureau of Mines in 1945 [9]. The first three tons of titanium sponge were produced by this method in the USA in 1948.

Titanium exhibits a valuable combination of high mechanical properties and comparatively low density ( $4.5 \text{ g/cm}^3$ ). Titanium alloys are distinguished by thermal stability and particularly high specific strengths (ratios of strength to density) at temperatures up to  $340\text{-}450^\circ\text{C}$ , and up to  $600^\circ\text{C}$  for the new alloys. Alloys that are stable at even higher temperatures ( $700\text{-}800^\circ\text{C}$ )

are under development. These qualities have made it possible to use titanium as a structural material in jet aviation, first for gas-turbine and jet engines, then for the airframe structures, and finally in rocket engineering.

Below we present brief essays on the titanium industries of the capitalist countries.

USA. Over the seven years from 1951 through 1957, several titanium plants were constructed in the USA with the active support of the government, which simultaneously guaranteed to buy their output.

The first titanium plant, which used the magnesiothermic method, was placed in operation by Titanium Metals Corporation of America (TMCA) in 1951 at Henderson, Nevada. Titanium production was accommodated in some of the buildings of a magnesium plant that had been erected during the Second World War and designed to produce 50 thousand tons of magnesium per year. In the new context, magnesium output was reduced to just meet the demands of titanium production. The firm does not now produce commercial magnesium. The original design output of the plant (5400 tons of titanium sponge) had been reached by 1956. The 4850-ton DuPont de Nemours titanium plant at Newport, Delaware had been placed in operation in 1954. This plant purchased outside magnesium for its magnesiothermic operations. Dow Chemical, the largest producer of magnesium in the USA, began titanium production in 1955. It built a 1600-ton-capacity plant at Midland, Michigan, where it had previously located one of its magnesium plants. The Kremet Incorporated Magnesiothermic Plant at Chattanooga, Tennessee, which has a 5400-ton capacity, was also placed in operation in 1955.

Under license from the British firm Imperial Chemical Industries (ICI), the firm Electrometallurgical (a subsidiary of Union Carbide) began construction in 1954 on the largest sodiothermic titanium plant in the USA - a 6750-ton installation at Ashtabula, Ohio. The plant began operations in April of 1956 and, according to published reports, had reached its planned performance by the

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end of that year. In 1957, another sodiothermic titanium plant was opened at Ashtabula by the National Distillers and Chemical Corporation. It has its own nearby sodium plant with a capacity of 27 thousand tons. According to available information, a new semicontinuous process is used at the titanium plant to produce the metal, but no details have been divulged [10].

In 1964, this firm joined with United States Steel Corporation to establish a new company - Reactive Metals, Incorporated, which was to engage in the production of titanium sponge, semi-finished titanium products, zirconium, and hafnium [11].

Construction of two more sodiothermic plants was reported during the ascendancy of the industry in the USA. The Columbia Southern Chemical Corporation, which produces titanium tetrachloride, proposed to join the British firm ICI as its licensee in the erection of a 4500-ton sodiothermic titanium plant at Natrium, West Virginia, which was to open in 1958. It was proposed that this plant be built on condition that financial support became available from the US Government. A new variant of the sodiothermic process was elaborated for the plant.

In 1956, the firms Kennecott Copper Corporation and Allied Chemical and Dye Corporation organized the Allied Titanium Corporation to construct a sodiothermic titanium plant with a capacity of 7300 tons at Wilmington, North Carolina. Proposals called for a continuous sodiothermic process at this plant, which was to be placed in operation in 1958-1959 [12].

Thus, the capacity of existing titanium plants and those under construction was to have been 24 thousand tons in 1956 and about 42 thousand tons in 1958.

Characteristically, the new plants were to be constructed exclusively for the sodiothermic method, and the relative output of the sodiothermic plants was accordingly to be increased steadily from 28% in 1956 to 48% in 1958.

The planned rapid development of the sodiothermic method of titanium production in the USA was based on technological and economic considerations that will be considered later in the part

of the book devoted to the technology of sodiothermic titanium production.

Up to 1957, the capacity of the American titanium industry increased rapidly. At the same time, it was repeatedly being predicted that world titanium production would rise significantly. For example, it was assumed that by 1960, the capacity of American plants would have increased to 200 thousand tons, and that by 1965 titanium might be produced in greater quantities than stainless steel and later come to rival aluminum output [13]. It was also supposed that increased titanium production would be encouraged by significant improvement of production methods, with the result that the prices of titanium and semifinished titanium products would drop almost to the level of those of stainless steels [13].

However, beginning in mid-1957, a sharp decrease in titanium-sponge production began in the USA and to a lesser degree in England and Japan, owing to a number of factors. The rapid development of the American titanium industry in the preceding years had been financed largely by the government. The government had been purchasing the production of titanium plants for stockpiling and military needs. Less than 10% of the titanium produced in 1956 was used. The sharp decline in interest in titanium was due to advances made in improving the properties of stainless steels, which are less expensive than titanium, to deficiencies in the production technology of semifinished titanium products (for some time, there were massive rejections due to high hydrogen contents in the pieces), to nonconformity of the titanium-based alloys that had then been developed (which had a sharp strength drop on heating above 420°C) to the new, more rigid specifications laid down for them, and to cuts in the program of military-aircraft construction in the context of improvements in rocketry, affecting primarily the production of B-52 heavy bombers, in whose production most of the titanium had been used. Early in 1958, the US government reversed its previous position, which had required firms producing semifinished titanium products to ship them preferentially to military installations. However, the nonmilitary

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Production of Titanium Sponge in the Capitalist Countries from 1949  
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TABLE 1  
 Production of Titanium Sponge in the Capitalist Countries from 1949  
 through 1966, Tons

| Year | USA   | Jap. | Eng. | total | Year | USA   | Jap. | Eng.  | total  |
|------|-------|------|------|-------|------|-------|------|-------|--------|
| 1949 | 23    |      |      | 23    | 1963 | 4160  | 1844 | 1179  | 6983   |
| 1950 | 68    |      |      | 68    | 1964 | 5436  | 2477 | 1100  | 7013   |
| 1951 | 49    |      |      | 49    | 1965 | 4818  | 3307 | 1180  | 8205   |
| 1952 | 975   | 3    |      | 978   | 1966 | 6103  | 3363 | 544   | 8910   |
| 1953 | 2033  | 70   |      | 2103  | 1967 | 6185  | 1529 | 773   | 7416   |
| 1954 | 4872  | 372  | 85   | 5650  | 1968 | 7157  | 1542 | 772   | 8671   |
| 1955 | 6712  | 1250 | 254  | 8216  | 1969 | 8200  | 3030 | 1000  | 12230  |
| 1956 | 12341 | 2311 | 1040 | 16752 | 1970 | 8200* | 4700 | 1000* | 13900* |
| 1957 | 15648 | 3078 | 1333 | 20259 | 1966 | 14500 | 6500 | 1000  | 22000  |

\*Estimated.

branches of US industry declined to use substantial amounts of titanium because of the lack of the required experience and the high cost of the metal.

The above factors resulted in a sharp drop in titanium production after 1957 (Table 1), suspension of construction work on new plants, and shutdowns of some of the existing plants: in 1960, titanium production was suspended at the Midland plant (Dow Chemical) and at Chattanooga (Kremet); in 1962, the plant at Ashtabula (Electrometallurgical) closed its doors.

The 1958-1960 recession in the USA was followed in 1961 by a new rise in titanium-sponge (Table 1) and semifinished titanium products output, primarily as a result of expanded use of titanium for military purposes and the development of high-speed airplane designs, such as the A-11, which is capable of 3200 km/h. Nevertheless, another titanium plant, the DuPont installation at Newport, closed in 1964 [14]. Thus, at the beginning of 1965, there were only two titanium-sponge producers left in the USA: the plant at Henderson, which used its own magnesium, and the one at Ashtabula, which used its own sodium.

The increased demand for titanium in the USA in recent years has revived the American titanium industry. For example, there are published reports to the effect that the capacity of the Ashtabula sodiothermic plant was increased from 2270 to 4500 tons in 1965 and would soon be raised to 6800 tons. It has been proposed that the plant's capacity be increased by another 70% by 1970 by the introduction of a continuous titanium production process that is now under development. The output of titanium ingots and semifinished products is to be increased simultaneously [15]. The capacity of the Henderson plant has been increased from 6350 to 9070 tons, thus compensating the decrease in overall output caused by the shutdown of the plant at Newport [16, 17]. Plans also call for doubling the capacity of the Henderson plant by 1970 [18]. It has been reported that the output of titanium sponge in 1964 (8200 tons) corresponded to 78% utilization of titanium-plant capacity [19] (this figure was 38% in 1960, 48% in 1961 and 1962, and 57% in 1963); in 1966, the titanium plants were in full-capacity

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operation at 14.5 thousand tons. Reports began to appear to the effect that four new firms proposed to go into titanium production [20]. At the end of 1965, the Oregon Metallurgical Corporation commissioned a pilot plant designed to produce titanium sponge [21], and construction was begun on an industrial complex capable of producing 1700 tons of sponge per year [118]. It is predicted that the annual demand for titanium sponge, including imports, will increase to 32 thousand tons by 1970 as compared with 20 thousand tons in 1966 [15].

With improvements of production technology, the cost of titanium sponge is dropping steadily. In 1953, 1 kg of grade A1 sponge was priced at \$11.01; the price was \$7.62 in 1956, \$4.02 in 1959, \$3.50 in 1963, and \$2.91 in 1964.

American sponge was being marketed at the same price in 1966 [117]. It is predicted that the price of the metal will be down approximately 20% by 1970 [15].

Although American titanium production in 1966 represented 87% of the 1957 output, the demand for semifinished titanium products was considerably higher than the 1957 level as early as 1962. For example, the production of titanium ingots had risen from 9.1 thousand tons in 1957 to 13.9 thousand tons in 1965 and 21.3 thousand tons in 1966, and the production of titanium rolled products had risen from 5.1 to 8.6 and 12.5 thousand tons, respectively. The technology of rolled-titanium production had been improved as a result of broad-scale research; rejection rates had been cut and scrap was utilized more effectively in smelting out the ingots [22, 121].

Development of a technology to produce highly purified titanium (99.9999%) for the electronics industry by the use of electron-beam remelting has been reported [23].

Japan. Titanium production was begun in Japan at a pilot plant of Osaka Titanium with a capacity of 18 tons per year. Subsequently, titanium-sponge production was organized by two other firms: Togo Titanium and Japan Soda. The latter firm, which produced about 150 tons of titanium sponge per year, suspended its

production in 1958. The capacities of the Osaka Titanium and Togo Titanium plants are about the same, at about 1500-2000 tons per year. Their annual outputs of sponge are also about the same. Other firms also have titanium pilot plants. Most of the titanium sponge produced is exported preferentially to the USA and a small part to Western Europe [24, 25].

The Japanese plants use the magnesiothermic method. Japanese titanium sponge is superior in quality to the American products. Most of the Japanese sponge has a Brinell hardness of about 100. However, this sponge is marketed in the USA at a price about 10% lower than that of the sponge produced in this country.

As a result of expanded export of titanium to the USA and Great Britain, the capacities of both Japanese titanium plants had increased to 3000 tons each by the beginning of 1966 [19, 26, 27].

Great Britain. Imperial Chemical Industries (ICI), the largest producer of sodium in England, began development of a technology to produce titanium by the sodiothermic method in 1951. The research was at first done in reactors designed to produce 3 and 45 kg of titanium, and then at a 150-ton-per-year pilot plant near Birmingham. Other methods were also tested simultaneously with the developmental work on the sodiothermic method - the magnesiothermic method, electrolysis, and reduction of titanium dioxide.

In mid-1955, less than two years after the start of construction, a 1500-ton titanium plant was placed in operation at Wilton, Yorkshire. The capacity of the plant was subsequently increased to 1800 tons. The titanium tetrachloride is supplied by British Titan Products at Billingham. In subsequent years, titanium production dropped off sharply and the demand for titanium was met basically with metal imported from Japan. At the end of 1964, there was another increase in titanium production at the Wilton plant [19]. Work is being completed to double the plant's titanium sponge production capacity [28].

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Other countries. According to published data, titanium sponge is being produced at pilot plants in France, Norway, Canada, West Germany, and Italy. For example, it has been reported that a small quantity of titanium in the form of tablets weighing from 5 to 7 g is being produced by Dominion Magnesium in Canada, which produces calcium in addition to magnesium. The titanium is produced by calcium reduction of titanium dioxides. The entire output is sent to Great Britain. Canada's domestic needs have been met by production of semifinished titanium products from ingots imported from the USA [29].

In 1961, an installation for titanium production by the two-stage sodiothermic method [30] was placed in operation in Italy.

In West Germany, pilot production of titanium has been set up by Titangesellschaft at Leverkusen.

The firm Kontimet, whose principals are three West German firms, including Krupp, and the American firm TMCA was organized in West Germany at the end of 1961. Kontimet engages in the production of semifinished products from imported titanium sponge. The possibility of its setting up the production of its own sponge has not been ruled out [31].

In France, titanium is produced by Societe' Titanium at a pilot plant in LePrese.

The total production of titanium sponge in the above countries is estimated at 500-600 tons per year.

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## Chapter 2

### THE PROPERTIES OF TITANIUM

Titanium has an atomic number of 22 and is an element of transitional group IV in D.I. Mendeleev's periodic system. The atomic mass of titanium is 47.90; its atomic volume is 10.7, and it has isotopes with mass numbers of 46, 47, 48, 49, and 50. New unstable titanium isotopes,  $Ti^{43}$ ,  $Ti^{45}$ , and  $Ti^{51}$  have recently been created.

Th

Titanium exists in two crystalline modifications, α and β. The polymorphic transformation temperature of titanium depends on the amount of impurities in it: for the pure metal, it is 882.5°C. The low-temperature modification (α-titanium) has a hexagonal lattice with dense packing of the atoms. The constants of the crystal lattice are  $a_0 = 2.95111 \text{ \AA} \pm 6 \cdot 10^{-5}$ ;  $c_0 = 4.68433 \pm 10 \cdot 10^{-5}$ ;  $c/a = 1.5873$  [32]. The lattice constants of α-titanium, and especially c, increase when small amounts of oxygen or nitrogen are absorbed, a process accompanied by the formation of solid solutions of oxygen and nitrogen in the titanium. The high-temperature modification (β-titanium) has a body-centered cubic lattice. Its constant a is  $3.3065 \pm 0.0001 \text{ \AA}$  at  $900 \pm 5^\circ\text{C}$ . The volume change on the α → β transformation is 5.5%.

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The density of pure α-titanium at 25°C is 4.507 g/cm<sup>3</sup>, that of β-titanium at 900°C is 4.32 g/cm<sup>3</sup>, and that of molten (commercial) titanium at the crystallization point is 4.11 g/cm<sup>3</sup>.

The temperature coefficient of linear expansion of titanium is  $10.7 \cdot 10^{-6}$  in the 20-700°C temperature range and  $6.8 \cdot 10^{-6}$  in the -190 to +20°C range [33].

The entropy of titanium at 25°C is 7.3 cal/(mole·deg), the latent heat of the  $\alpha + \beta$  transformation is 0.83 kcal/mole, the melting point is  $1660^\circ\text{C} \pm 4$ , the latent heat of fusion 4.5 kcal/mole, the boiling point 3260°C, the latent heat of evaporation (at the boiling point) 102.5 kcal/mole, the specific heat of  $\alpha$ -titanium is  $5.28 + 2.4 T \cdot 10^{-3}$  cal/(mole·deg), that of molten titanium is -8.00 cal/(mole·deg), and that of the vapor phase is 5.84 cal/(mole·deg) [34]. The heat capacity of  $\beta$ -titanium is determined from the equation [35]

$$C_p = 4.61 + 1.917 \cdot 10^{-3} \text{ cal/(mole·deg)}. \quad (1)$$

The equation

$$\lg P_{\text{sat}} = 7.30 - \frac{24200}{T} \quad (2)$$

has been proposed for the vapor pressure of titanium in the temperature range from 1377 to 1537°C.

Titanium has a surface tension of  $1588 \text{ dynes}\cdot\text{cm}^{-1}$  at the melting point. Impurity contents in the metal, in %: 0.008 Fe, 0.002 Al, 0.0001 Mn [36].

According to some sources, the thermal conductivity coefficient of titanium decreases with increasing temperature from  $3.7 \times 10^{-2} \text{ cal/(cm}\cdot\text{s}\cdot\text{deg}^{-1})$  at 50°C to  $3.1 \cdot 10^{-2} \text{ cal/(cm}\cdot\text{s}\cdot\text{deg}^{-1})$  at 700°C; according to other sources, it is  $4.06 \cdot 10^{-2}$  at 0° and  $3.55 \cdot 10^{-2}$  at 300°C; beginning at this temperature, it rises to  $3.7 \cdot 10^{-2} \text{ cal/(cm}\cdot\text{s}\cdot\text{deg}^{-1})$  at 600°C.

The resistivity of titanium at 20°C is about  $42 \cdot 10^{-6} \Omega\cdot\text{cm}$ ; it approximately triples toward 800°C, and according to other sources it is  $182 \cdot 10^{-6} \Omega\cdot\text{cm}$  at the  $\alpha + \beta$  transition, i.e., at 882°C. Titanium has a temperature coefficient of resistivity of  $5.5 \cdot 10^{-3} \Omega\cdot\text{cm/deg}$  [37].

TABLE 2  
Influence of Temperature on the Mechanical Properties  
of Titanium  
(Cold-rolled sheet reduced 50%)

| Temp.,<br>°C | $\sigma_b$ , kgf/mm <sup>2</sup> | $\sigma_{0.2}$ , kgf/mm <sup>2</sup> | $\delta$ , % | $\psi$ , % | $\epsilon$ , kgf/mm <sup>2</sup> |
|--------------|----------------------------------|--------------------------------------|--------------|------------|----------------------------------|
| 204          | 67                               | 52                                   | 18           | 38         | 0600--10500                      |
| 428          | 37                               | 35                                   | 46           | 65         | 9100--9800                       |
| 537          | 14                               | 12                                   | 79           | —          | 7300--8000                       |

Titanium is paramagnetic; its mass susceptibility is  $(3.2 \pm 0.4) \cdot 10^{-6}$  [38]. The coefficient of Hall effect for  $\alpha$ -titanium is  $(+1.82 \pm 0.2) \cdot 10^{-13}$  [33].

The chemical composition and mechanical properties of titanium sponge are determined to a substantial degree by the method used to produce it, and by the technology used to purify the reaction mass. The most characteristic data on the chemical composition and mechanical properties of titanium sponge produced by metallothermic methods are given in Chapters 14 and 16. These chapters also include data on the influence of the main impurities on the mechanical properties of titanium sponge.

The influence of temperature on the mechanical properties of titanium is indicated in Table 2.

Titanium is distinguished by low creep resistance in spite of its high recrystallization and melting points. Annealed titanium has the strongest tendency to creep. Cold rolling increases the creep resistance of titanium, as well as its yield point. A creep rate of 0.0001%/h is reached under a stress representing 80% of the yield point in cold-rolled titanium and at 50-60% of the yield point in the annealed material. The creep rates of titanium and other structural materials are compared in Fig. 1.

It follows from these data that the yield point cannot be used as a design characteristic for titanium, especially when it is necessary to apply static loads over the long term. Titanium can be used when stresses near the yield point operate only briefly. Titanium-based alloys exhibit higher resistance to creep, and this property can be improved still further by heat treatment.

TABLE 3  
 Mechanical Properties of Titanium Compared with Those of Other High-Melting Metals and Structural Alloys

| property   | titanium               | zirconium             | tantalum              | soft steel<br>0.1% C<br>0.05% S | type 18-8<br>stainless<br>steels | copper-beryllium<br>alloy<br>(2-2.5% Be) |
|--|------------------------|-----------------------|-----------------------|---------------------------------|----------------------------------|--|
| elastic modulus, kgf/mm <sup>2</sup>   | 1.18 · 10 <sup>4</sup> | 0.8 · 10 <sup>4</sup> | 1.9 · 10 <sup>4</sup> | —                               | —                                | 1.27 · 10 <sup>4</sup>                   |
| ultimate strength, kgf/mm <sup>2</sup> :<br>after annealing                                      | 57.6                   | 29.5-49.2             | 34.6-35.2             | 35.2-42.2                       | 59.4-66.9                        | 49.2                                     |
| after cold working   | 88.8                   | 31.0-40.8             | below 70.4            | below 63.4                      | 148.0                            | 120.0                                    |
| yield point, kgf/mm <sup>2</sup> :<br>after annealing  | 43.6                   | 11.2-21.3             | —                     | 21.1                            | 21.1-24.6                        | 21.8                                     |
| after cold working   | 70.4                   | 25.4-34.5             | —                     | 42.2                            | —                                | 95.0                                     |
| elongation, %:<br>after annealing  | 28.0                   | 26.5                  | 50.0                  | 35                              | 55-60                            | 45                                       |
| after cold working   | 4                      | below 6.6             | below 8               | 10-15                           | 22                               | 3-6                                      |
| hardness HB:<br>after annealing  | 100                    | 85                    | 70-150                | 90-100                          | 140-180                          | 110                                      |
| after cold working   | 207                    | —                     | below 200             | below 200                       | —                                | 340                                      |
| specific strength (ratio of strength<br>in kgf/mm <sup>2</sup> to density in g/cm <sup>3</sup> ) | 19.65                  | 15.7-15.3             | below 1.85            | —                               | 18.65                            | 14.6                                     |

<sup>1</sup>Data for wrought titanium containing 0.15% Fe, 0.02% Si, 0.05% O<sub>2</sub>, 0.05% N<sub>2</sub>, and 0.04% Ca.

TABLE 4  
 Chemical Composition of Technical Titanium and Metal Refined by the  
 Iodide Method

| Impurity | content, 10 <sup>-4</sup> % |                    | content, 10 <sup>-4</sup> % |                    | content, 10 <sup>-4</sup> % |                    |
|----------|-----------------------------|--------------------|-----------------------------|--------------------|-----------------------------|--------------------|
|          | iodide titanium             | technical titanium | iodide titanium             | technical titanium | iodide titanium             | technical titanium |
| Al       | 34                          | 34                 | 0.6                         | <0.07              | 11                          | 11                 |
| As       | 1.2                         | <0.04              | 0.3                         | <0.1               | 3.3                         | <0.13              |
| B        | 0.07                        | 6.07               | 0.7                         | <0.08              | 129                         | 3                  |
| Ca       | 4                           | 4                  | 1.1                         | 1.6                | 56                          | 0.1                |
| Co       | 0.6                         | <0.1               | 0.7                         | 2.5                | 0.1                         | <0.09              |
| Cu       | 8.7                         | 3.3                | 3.6                         | 0.25               | <0.3                        | 5                  |
| Cr       | 5.3                         | 3.5                | 0.5                         | 3                  | 1.4                         | 100                |
| Fe       | 200                         |                    | 0.63                        |                    | 83                          | 44                 |

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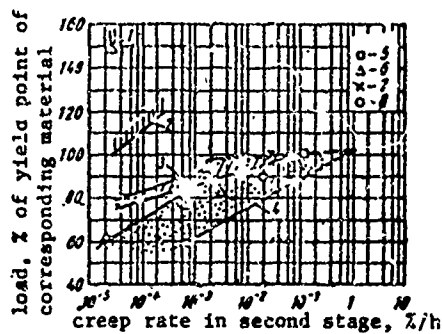


Figure 1. Comparison of minimum creep rates of titanium and other structural metals. 1) Normalized low-carbon steel; 2) 18-8 stainless steel; 3) scattering range for cold-rolled titanium; 4) scattering range for annealed titanium; 5) annealed titanium sheet, with the grain; 6) annealed titanium sheet, across the grain; 7) cold-rolled titanium strip, with the grain; 8) cold-rolled titanium strip vacuum-annealed at 818°C, across the grain.

The chemical stability of titanium will be discussed below, along with the properties of titanium-based alloys.

The mechanical properties of iodide titanium:  $\sigma_b = 26.7-33.7$  kgf/mm<sup>2</sup>,  $\sigma_s = 14.0-16.9$  kgf/mm<sup>2</sup>,  $\delta = 40-55\%$ ,  $\psi = 60-75\%$ ,  $E = 10,900$  kgf/mm<sup>2</sup>, hardness 73 H<sub>b</sub> [33]. Table 3 compares the mechanical properties of titanium with those of other high-melting metals and structural alloys [33].

Comparatively detailed analyses of technical titanium and metal refined by the iodide method are given in Table 4 [32].

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## Chapter 3

### BASIC INFORMATION ON TITANIUM ALLOYS

It follows from the data given above that titanium exhibits high strength and hardness and good plasticity combined with low density. As Table 3 shows, the specific strength of titanium is superior to that of many structural materials. Titanium also has a high melting point, a necessary condition for acquisition of alloys with high hot strength. The small linear expansion coefficient of titanium enables it to perform reliably under temperature-cycling conditions. Its excellent corrosion resistance makes it possible to use titanium in many aggressive environments.

As regards its machinability, titanium resembles type 18-8 stainless steel; it can be subjected to all types of mechanical working and can be welded in various ways (with certain precautionary measures). The surfaces of titanium products can be strain-hardened by various methods and oxide films can be formed on them electrolytically.

Along with its advantages, titanium has a number of shortcomings. One of them is its low modulus of normal elasticity, which makes it difficult to design rigid and stable structures. In many cases, this makes it necessary to design heavier products, with the result that the weight economy associated with the low density of titanium is lost [38]. In certain cases, however, the

comparatively moderate elastic moduli of titanium and its alloys can be regarded as an advantage, since it enables us, for example, to lower the stresses that arise under alternating loads and the magnitude of the thermal stresses that arise when the structure is heated. The low thermal conductivity of titanium has a detrimental influence on its use properties, lowering thermal-cycle stability. This deficiency is offset to a certain degree by the metal's small coefficient of linear expansion.

As we noted above, titanium exhibits creep not only at elevated, but also at room temperatures. Increases in aircraft speeds and the development of rocket engineering, where the use of titanium is particularly attractive because of its low density, require a substantial increase in the mechanical strength of titanium at elevated temperatures, or, in other words, the development of titanium alloys with higher hot strength. It also came to be required of titanium that it exhibit certain properties at extremely low temperatures.

At the present time, titanium is used preferentially not in the technical form, but in titanium-based alloys. The polymorphism of titanium, the good solubility of many elements in it, and the formation of chemical compounds with variable solubility make it possible to use titanium as a base for many alloys with a variety of structures and properties. For example, the ultimate strength of titanium can be raised by alloying and heat treatment from 50 kgf/mm<sup>2</sup> in unalloyed titanium to 150 kgf/mm<sup>2</sup> and higher in modern heat-hardenable alloys. Ultimate strengths of 150 kgf/mm<sup>2</sup> and higher are attainable only in special high-alloy steels. However, if their specific strengths are compared with those of titanium alloys, the latter are found to have the advantage, since they are superior to all other structural materials in this respect. The specific strengths of titanium alloys range up to 33.4, and those of high-strength structural steels to 19.2. To compare with the titanium alloys in specific strength, a steel would have to have an ultimate strength of the order of 250-260 kgf/mm<sup>2</sup>. However, such a steel would lack technological plasticity. The superiority of titanium alloys over high-strength

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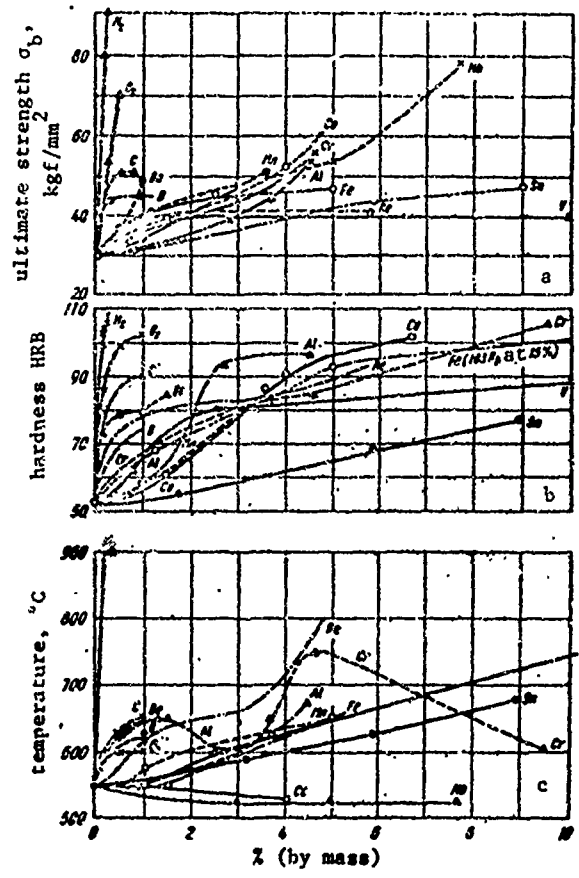


Figure 2. Influence of alloying additives on:  
 a) ultimate tensile strength of iodide titanium;  
 b) hardness of iodide titanium;  
 c) recrystallization point of iodide titanium.

steels, and over aluminum and magnesium alloys as well, persists over a broad temperature range - up to 400-500 and even 600°C. At 300-350°C, titanium alloys are ten times stronger than aluminum alloys, and existing aluminum and magnesium alloys are totally useless at higher temperatures.

As a result of research conducted over the last few years, it has been established that the working temperatures of titanium alloys can be raised substantially, and in some cases brought close to those of iron- and nickel-based hot-strength alloys [38].

Titanium is capable of dissolving almost all elements of the periodic system. At the present time, however, aluminum, chromium, molybdenum, vanadium, manganese, tin, copper, niobium, tantalum, iron, tungsten, and silicon are of the greatest practical importance as alloying additives to titanium. They form substitutional solid solutions with titanium. Figure 2 shows the effects of certain alloying elements on the mechanical properties of titanium.

The basic nonmetallic impurities, which include oxygen, nitrogen, hydrogen, and carbon, form interstitial solid solutions with titanium. Dissolving in the metal, they distort its crystal lattice, increase interatomic-bond rigidity, and lower the capacity of the granules for plastic deformation. As a result, the hardness and strength of titanium increase under the influence of these impurities, and its plasticity decreases. To secure an additional strength increase in titanium, its oxygen content is sometimes increased, as by introducing a calculated amount of titanium dioxide into the charge in the ingot-making process [40]. The same effect is obtained by introducing a certain amount of oxygen-enriched scrap into the ingot charge (see Chapters 20 and 21).

An oxygen impurity raises the melting point of titanium. It is a highly active  $\alpha$ -stabilizer and raises the temperature of the allotropic transformation by a substantial margin. Oxidation of titanium begins in an oxygen environment at 250°C and accelerates with rising temperature [41]. The laws governing the

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oxidation of titanium in air and oxygen are complex, because of the large number of oxides that exist in the titanium-oxygen system and because of titanium's large capacity for dissolved oxygen. On heating to 1100°C in oxygen, titanium oxidizes at a substantially higher rate than it does in air, but the situation is reversed above this temperature. To a certain extent, this is because of the lower diffusion rates of nitrogen and titanium nitride in titanium, but the lower stability of titanium nitride as compared with the oxides of titanium is also a factor.

The oxidation resistance of titanium increases when it is alloyed with aluminum and tungsten and also when it is given thermally diffused coatings of aluminum, boron, silicon, and beryllium.

A number of studies have been devoted to determining the conditions under which an explosive reaction occurs between titanium and oxygen. It has been established that the basic factor causing ignition of titanium in oxygen is failure of the oxide film on the titanium, which allows oxygen free access to the surface of the metal. The titanium-oxidation reaction rate depends on the oxygen pressure in the system, temperature, the degree of dispersion of the titanium, and the presence of alloying additives in it.

A certain critical pressure corresponds to each temperature; at this pressure, the rate of formation of titanium oxide is so high that a disordered structure that does not inhibit the development of the oxidation reaction is formed. Fine-grained titanium (53-75  $\mu$ m) ignites in oxygen at standard pressure and 520°C; for the alloys with manganese, the ignition point rises to 680°C at a manganese content of 10-12%; alloying with aluminum raises the ignition point of the powder even further than does manganese [42]. The critical pressure for ignition of titanium chips at 150°C in oxygen is 3 atm, or 1 atm in air at 1000°C [43].

The critical oxidation pressure required to ignite compact titanium with no protective oxide film, e.g., on a fresh crystalline fracture, is 8 atm at 300°C and 1.4 atm at 1000°C [44]. In

contact with liquid oxygen, titanium ignites only when some of the oxygen vaporizes at the titanium surface, as under the influence of heat generated on impact [45].

Oxygen dissolves irreversibly in titanium and is practically impossible to remove from the metal, although there have been a number of proposals and patents on this problem.

Hydrogen is a detrimental impurity in titanium in practically any quantity, since it lowers impact strength substantially and increases notch sensitivity sharply.

The figure usually cited as a permissible hydrogen content in titanium is 0.012-0.015%; the content should be held at or below 0.007% to ensure good properties in the titanium.

Depending on temperature, as much as 1.5 to 2% of hydrogen may dissolve in titanium. Its solubility in  $\alpha$ -titanium at 325°C is about 0.2%, but it drops practically to zero at room temperature. All of the hydrogen is then bound in the  $\gamma$ -phase, which is titanium hydride. Because of the higher (by several times) solubility of hydrogen in  $\beta$ -titanium as compared with  $\alpha$ -titanium, its detrimental influence on two-phased ( $\alpha + \beta$ ) alloys or on alloys with the  $\beta$ -structure is weaker than in the case of single-phase  $\alpha$ -alloys, since practically all of the hydrogen in alloys with the  $\alpha$ -structure goes to form titanium hydrides, which precipitate out along grain boundaries or in the grains and embrittle the material. In alloys with the ( $\alpha + \beta$ )- or  $\beta$ -structure, a considerable part of the hydrogen is dissolved in the  $\beta$ -phase and no structurally free hydrides are formed [38].

Unlike oxygen and nitrogen, which dissolve irreversibly in titanium, hydrogen can be removed from the metal by heating in a vacuum to temperatures above 650°C. The degasification process accelerates substantially as the temperature is increased.

The presence of an electroplated coating or oxide film on the surface of titanium retards degasification, whose rate is determined by the rate of the process unfolding on the surface of the metal and involving the escape of hydrogen atoms from it.

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Nitrogen has a stronger effect on titanium than oxygen, and its content as a harmful impurity must therefore be smaller than the permissible oxygen content.

Like oxygen, nitrogen is a highly active  $\alpha$ -phase stabilizer and raises the temperature of the allotropic transformation very sharply.

Both nitrogen and oxygen increase the constant  $c$  of the  $\alpha$ -phase crystal lattice substantially and have almost no effect on the constant  $a$ . The  $c/a$  ratio increases, strength is improved substantially, and the plasticity of the material is lowered [38].

The interaction of titanium with nitrogen at temperatures from 20 to 300°C was studied by V.V. Sergeyev and L.L. Neroslavskaya [47]. The experiments were made with titanium powder in grain sizes of  $-2.5 + 1.6$  mm [sic] prepared by electrolytic refining of sponge scrap. In the presence of oxygen, titanium undergoes insignificant nitrogen saturation in the 20-300°C temperature range. As subsequent temperature rise to 400°C and holding in air for one hour results in a sharp increase in the nitrogen content of the titanium, to 0.04%, and to 0.07% at 500°C. It is obvious that an oxide film first forms in air and protects the titanium from interacting with nitrogen to a considerable degree. The film structure begins to break up at 400°C, and this permits more vigorous reaction between the surface layers of the titanium and the nitrogen.

Absorption of nitrogen from a nitrogen atmosphere is pronounced at 50°C. When the temperature is raised to 150°C, the rate at which titanium absorbs nitrogen rises markedly. A further temperature rise to 500°C has little influence on nitrogen saturation of titanium, apparently because of the low solubility of the nitride film in the titanium.

The chemical compositions and conventional designations of Soviet structural titanium alloys are given in Table 5, and their mechanical and physical properties in Table 6 [48].

The technological properties of titanium alloys are related to their structures. The structure may be that of the pure  $\alpha$ -

TABLE 5  
Chemical Composition and Conventional Designations of  
Soviet Titanium-Based Alloys

| designa-<br>tion of<br>alloy | basic components, % |            |         |         |             | impurities, %, not above |          |      |
|------------------------------|---------------------|------------|---------|---------|-------------|--------------------------|----------|------|
|                              | Mn                  | Mo         | Cr      | Al      | V           | Fe                       | N        | O    |
| VT3                          | —                   | —          | 2.0-3.0 | 4.0-6.2 | —           | 0.3                      | 0.4      | 0.2  |
| VT3-1                        | —                   | 1.5-2.5    | 1.5-2.5 | 5.0-6.3 | 0.1-0.5 Fe  | —                        | 0.15-0.3 | 0.2  |
| VT4                          | 0.8-2.0             | —          | —       | 3.5-5.0 | —           | 0.4                      | 0.15     | 0.15 |
| OT4                          | 0.8-2.0             | —          | —       | 2.0-3.5 | —           | 0.4                      | 0.15     | 0.15 |
| OT4-1                        | 0.8-2.0             | —          | —       | 1.0-2.5 | —           | 0.4                      | 0.15     | 0.15 |
| VT5                          | —                   | —          | —       | 4.0-5.5 | —           | 0.3                      | 0.15     | 0.15 |
| VT5-1                        | 2.0-3.0 Sn          | —          | —       | 4.0-5.5 | —           | 0.3                      | 0.15     | 0.2  |
| VT6                          | —                   | —          | —       | 4.5-6.5 | 3.5-4.5     | 0.3                      | —        | 0.15 |
| VT6                          | —                   | 2.8-3.8    | —       | 5.8-6.0 | 0.2-0.35 Si | 0.4                      | —        | 0.15 |
| VT14                         | —                   | 2.8-3.8    | —       | 3.5-4.5 | 0.7-1.5     | 0.4                      | 0.15     | 0.15 |
| VT15                         | —                   | 7.8        | 10-11.5 | 2.5-3.5 | —           | 0.3                      | 0.15     | 0.15 |
| VT10**                       | 2.0-3.0 Sn          | 2.8-3.5 Cu | —       | 5.0-6.0 | —           | 0.3                      | 0.2      | 0.2  |

\*All of the alloys may contain no more than 0.1% C, 0.05% N<sub>2</sub>, and 0.015% H<sub>2</sub>.

\*\*Composition according to [58].

phase, the pure β-phase, a mixture of these phases, a eutectoid, or chemical compounds. All alloying elements can be broken down into three groups on the basis of their influence on the polymorphic transformation in titanium: α-stabilizers, which raise the temperature of this transformation, β-stabilizers, which lower it, and alloying additives that have little influence on this temperature and are known as neutral hardeners. Figure 3 [49] presents a classification of alloying elements based on this criterion. The α-stabilizer used in practice is aluminum; β-stabilizers include iron, chromium, molybdenum, and certain other metals; tin and zirconium are neutral hardeners. Titanium alloys can be classified roughly into three groups in accordance with the above.

Alloys with the α-structure. These include the VT5 and VT5-1 alloys. The most important property of alloys with the α-structure is their good weldability by argon-shielded arc welding and

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TABLE 6

Basic Mechanical and Physical Properties of Soviet Titanium-Based Alloys

| Property  | alloy designation |        |             |             |           |        |           |           |
|---|-------------------|--------|-------------|-------------|-----------|--------|-----------|-----------|
|   | VT3               | VT3-1  | VT4         | VT4         | VT5       | VT6    | VT8       | VT14      |
| ultimate strength, kgf/mm <sup>2</sup>                            | 95-115            | 95-120 | 80-90       | 70-85       | 90-95     | 90-100 | 105-118   | 115-140   |
| yield point, kgf/mm <sup>2</sup>                                  | 85-105            | 85-110 | 70-80       | 55-65       | 70-85     | 80-90  | 95-110    | 108-130   |
| terminal elongation, %  | 10-18             | 10-16  | 15-22       | 15-30       | 12-25     | 9-13   | 9-15      | 6-10      |
| necking ratio, %  | 25-40             | 25-40  | 20-30       | 25-35       | 31-45     | 30-45  | 30-55     | —         |
| impact strength, kgf·m/cm <sup>2</sup>                            | 3-6               | 3-6    | —           | 3.5-6.5     | 3-6       | 4-8    | 3-6       | 2.5-3.5   |
| Rockwell hardness, HR <sub>C</sub>                                | 27-36             | 27-36  | —           | 60-70*      | —         | —      | 310-350** | 340-370** |
| elastic modulus, kgf/cm <sup>2</sup>                              | 11000             | 11500  | 11000-12000 | 11000-12000 | 10100     | 11300  | 11000     | 11000     |
| shear modulus, kgf/mm <sup>2</sup>                                | 4250              | 4370   | 4200        | 4000        | 4250      | —      | 4250      | —         |
| Poisson's ratio   | 0.3               | 0.3    | 0.31        | —           | 0.3       | —      | 0.3       | —         |
| ultimate shear strength, kgf/mm <sup>2</sup>                      | 65-70             | 65     | —           | —           | 65        | —      | 65-70     | —         |
| endurance limit, 10 <sup>7</sup> -cycle base, kgf/mm <sup>2</sup> | 45                | 48     | —           | —           | 27***, 48 | 30     | 50        | 44        |
| density, g/cm <sup>3</sup>  | 4.85              | 4.5    | 4.5         | 4.55        | 4.5       | 4.43   | 4.47      | 4         |
| resistivity, Ω·mm <sup>2</sup> /m                                 | 1.58              | 1.36   | —           | —           | 1.08      | 1.6    | 1.61      | —         |
| coefficient of linear expansion x 10 <sup>6</sup><br>(20-100°C)   | 8.4               | 8.6    | —           | 8.0         | 8.41      | 8.4    | 8.4       | 8.0       |
| thermal conductivity (at 25°C),<br>cal/(cm·s·deg)                 | 0.017             | 0.019  | 0.02-0.03   | 0.02        | 0.018     | 0.018  | 0.017     | 0.020     |

\*B scale.  
\*\*Brinell.  
\*\*\*Sheet.

TABLE 6  
 Basic Mechanical and Physical Properties of Soviet Titanium-Based Alloys  
 Property  
 ultimate strength, kgf/mm<sup>2</sup>  
 yield point, kgf/mm<sup>2</sup>  
 terminal elongation, %  
 necking ratio, %  
 impact strength, kgf·m/cm<sup>2</sup>  
 Rockwell hardness, HR<sub>C</sub>  
 elastic modulus, kgf/cm<sup>2</sup>  
 shear modulus, kgf/mm<sup>2</sup>  
 Poisson's ratio  
 ultimate shear strength, kgf/mm<sup>2</sup>  
 endurance limit, 10<sup>7</sup>-cycle base, kgf/mm<sup>2</sup>  
 density, g/cm<sup>3</sup>  
 resistivity, Ω·mm<sup>2</sup>/m  
 coefficient of linear expansion x 10<sup>6</sup>  
 (20-100°C)  
 thermal conductivity (at 25°C),  
 cal/(cm·s·deg)

their high thermal stability, i.e., the absence of embrittlement during prolonged subjection to high temperatures and stresses. In some cases, these alloys retain adequate strength up to 650°C. They resist gas corrosion in air up to 1090°C and can therefore be pressure-worked at high temperatures. The shortcomings of these alloys include lower technological plasticity as compared with those of the second and third groups and the fact that they cannot be strengthened by heat treatment. Alloys with the  $\alpha$ -structure are used to make forgings, extrusions, and various shapes for welding.

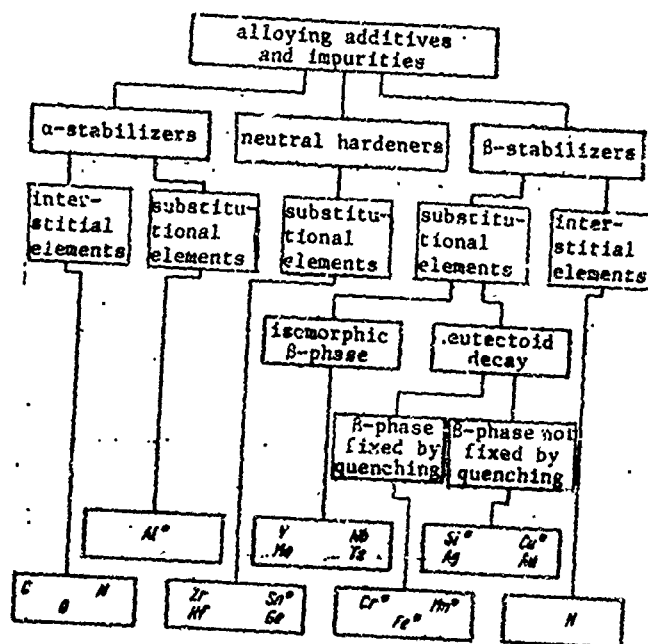


Figure 3. Diagram showing classification of alloying elements for titanium. The asterisked may produce hot-strength alloys with inter-metallic hardening.

Alloys with the  $\alpha + \beta$ -structure. This group includes alloys of the martensite type, in which the  $\beta$ -phase exists only at elevated temperatures, and two-phased alloys, in which the  $\beta$ -phase

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may persist in certain quantities even at room temperature. Martensite-type alloys contain aluminum as the predominant alloying additive and a small amount of a  $\beta$ -stabilizer. This group includes the alloys OT4-1, OT4, and VT4. They have approximately twice the strength of unalloyed titanium, but retain it only up to about 430°C. To a substantial degree, these alloys retain the advantages of  $\alpha$ -structured alloys; their weldability and thermal stabilities are rather good. Owing to the appearance of the ductile  $\beta$ -phase at comparatively moderate heating temperatures, the alloys of this group are easier technologically and pressworking produces better results. Alloys OT4 and OT4-1 are now the most commonly used sheet alloys. The martensite-type alloys have a drawback in that they have no capacity for hardening heat treatment.

A further increase in the  $\beta$ -stabilizer content produces two-phased alloys with higher strength properties at room and elevated temperatures but poorer response to welding than the martensite-type or  $\alpha$ -structured alloys. For this reason, the two-phased alloys are used for the production of all types of semi-finished products.

The group of two-phased alloys includes the hot-strength alloys VT3, VT3-1, VT6, VT8, and VT14. The VT6 alloy can also be used in the form of sheets, since it is the most easily welded alloy of the two-phased subgroup. The VT3-1 and VT6 two-phased alloys can be hardened by quenching and aging.

Alloys with the  $\beta$ -structure. This group includes titanium alloys into which so much  $\beta$ -stabilizer has been injected that they consist entirely of the  $\beta$ -phase after quenching or even after annealing. Alloy VT15 belongs to this group.

Alloys with the  $\beta$ -structure offer great promise for further development, since they combine good technological plasticity with very high strength and excellent weldability. In the as-quenched state, they submit well to all shape-changing operations (bending, stamping), and this makes it possible to use them to fabricate complex-shaped products. These products can be endowed with high

strength by artificial aging. As a result, strengths of 140-150 kgf/mm<sup>2</sup> coupled with satisfactory workability are well within reach for the  $\beta$ -structured alloys.

TABLE 7

Mechanical Properties of Titanium Alloys at Elevated Temperatures

| alloy designation | test temp., °C | mechanical properties            |                                  |              |                           | recommended max. temp. for long-term service, °C |
|-------------------|----------------|----------------------------------|----------------------------------|--------------|---------------------------|--|
|                   |                | $\sigma_b$ , kgf/mm <sup>2</sup> | $\sigma_s$ , kgf/mm <sup>2</sup> | $\delta$ , % | $E$ , kgf/mm <sup>2</sup> |  |
| VT1 <sup>0</sup>  | 300            | 22                               | 14                               | 26.8         | —                         | <300   |
|                   | 400            | 20                               | 11                               | 29           | —                         |  |
|                   | 500            | 17                               | 8                                | 37           | —                         |  |
|                   | 600            | 6                                | 5                                | 70           | —                         |  |
| VT3               | 300            | 67                               | 53                               | 11           | 9600                      | 500  |
|                   | 400            | 64                               | 50                               | 12           | 8500                      |  |
|                   | 500            | 57                               | 41                               | 14           | 7300                      |  |
| VT3-1             | 300            | 65                               | 56                               | 14           | 9000                      | 500  |
|                   | 400            | 60                               | 49                               | 14           | 8500                      |  |
|                   | 450            | 58                               | 47                               | 14           | 8300                      |  |
|                   | 500            | 56                               | 42                               | 15           | 8000                      |  |
| VT5               | 300            | 53                               | 43                               | 11           | 8700                      | 400  |
|                   | 400            | 48                               | 40                               | 14           | 7800                      |  |
| VT6               | 400            | 58                               | 47                               | 9            | —                         | 400  |
|                   | 500            | 50                               | 30                               | 16           | —                         |  |
| VT8               | 400            | 75                               | 61                               | 8            | 9800                      | 550  |
|                   | 500            | 72                               | 57                               | 8            | 9000                      |  |
|                   | 600            | 60                               | 32                               | 9            | 7900                      |  |

\*With the grain.

The development of heat-hardenable alloys is an important trend in titanium-alloy development, especially for semifinished sheet products; assimilation of such alloys will make it possible to broaden the field of application of titanium [38].

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The mechanical properties of certain titanium alloys at elevated temperatures are listed in Table 7 [38]. The characteristics of unalloyed titanium (VT1) are given for comparison.

The maximum use temperature of a given titanium alloy, which corresponds to the temperature at which it recrystallizes, can be determined tentatively by A.A. Bochvar's formula

$$T_r = kT_m,$$

where  $T_r$  is the recrystallization temperature in °K and  $T_m$  is the melting point in °K.

For technically pure titanium,  $k = 0.36$ ; the value of  $k$  can be increased to 0.5 by alloying the titanium, e.g., with 8% Al and 4% Mo. This raises the maximum use temperature of this alloy from 420 to 690°C.

The possibilities of alloying titanium to increase the coefficient  $k$  are still far from exhausted. Development of titanium-based alloys capable of working over the long term at temperatures of 850-900°C is a distinct possibility [38]. Some Soviet scientists take the view that the normal and high-temperature strengths of titanium alloys increase when a solid solution containing many atoms of different species is present in them.

Certain titanium alloys are subject to requirements calling for retention of high mechanical properties at cryogenic temperatures.

At -196°C, alloys VT5 and VT6 show a substantial increase in ultimate strength (140 and 165 kgf/mm<sup>2</sup>, respectively), but their terminal elongations decline to 3%. However, there are known alloys that exhibit high plasticity and toughness at -196°C. For example, the mechanical properties of the ternary alloy with 4% Al and 4% V at this temperature were found to be as follows:  $\sigma_b = 149$  kgf/mm<sup>2</sup>,  $\delta = 10\%$ ,  $\psi = 34.5\%$ ,  $a_k = 5.5$  kgf·m/cm<sup>2</sup>. An alloy of titanium with aluminum and molybdenum also retains good mechanical characteristics at this temperature [50].

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Aluminum is also one of the basic alloying components in American titanium alloys. In some alloys, iron is injected as an alloying additive. One of the alloys is injected with 0.25% of oxygen in addition to chromium and iron. There are alloys with numerous alloying components, each present in a modest content; as an example, we might mention Ti-155A, whose composition is Ti-5.5Al-1.5Cr-1.5Mo-1.5Fe.

Many American alloys with the  $\alpha$ -structure contain small (1-2%) additives of one or two isomorphous  $\beta$ -stabilizers: vanadium, molybdenum, niobium, or tantalum. It has been reported that small cobalt and silicon additives improve multicomponent alloys. The alloys Ti-6Al-4V; Ti-5Al-2.5Sn; Ti-13V-11Cr-3Al; Ti-8Al-1Mo-1V; Ti-6Al-6V-2Sn; Ti-5Al-5Sn-5Zr and others have come into extensive use. More than 25 different alloys are produced on an industrial scale [49, 51-53].

TABLE 8  
Mechanical Properties of Certain American Titanium Alloys at Normal Temperatures

| alloy designation | mechanical properties            |                                  |              |                                  |
|-------------------|----------------------------------|----------------------------------|--------------|----------------------------------|
|                   | $\sigma_b$ , kgf/mm <sup>2</sup> | $\sigma_s$ , kgf/mm <sup>2</sup> | $\delta$ , % | $\epsilon$ , kgf/mm <sup>2</sup> |
| A 110-AT          | 81                               | 77                               | 18           | 11600                            |
| MST-8Mn           | 98                               | 91                               | 12           | 10970                            |
| C-130AM           | 98                               | 91                               | 10           | 10545                            |
| Ti-155A           | 107                              | 84                               | 12           | 11250                            |
| MST-2.5 Fe-2.5V   | 98                               | 91                               | 12           | 10500                            |
| Ti-140A           | 98                               | 90                               | 12           | --                               |
| Ti-155AX          | 109                              | 98                               | 12           | --                               |
| MST-2Al-2Fe       | 102                              | 95                               | 12           | 11600                            |
| 5Al-5Sn-5Zr       | 96                               | 79                               | 18           | 11800                            |
| 6Al-6V-2Sn        | 112                              | 98                               | 13           | 11980                            |
| 8Al-1Mo-1V        | 107                              | 100                              | 15           | 12660                            |
| 13V-11Cr-3Al      | 96                               | 93                               | 15           | 10530                            |

The mechanical characteristics of certain American titanium alloys appear in Table 8 [38, 54].

In 1965-66, the USA produced titanium and titanium-alloy semifinished products in the following relative quantities:

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forgings and stamped blanks 55-57%; plates, sheets, and ribbon 19-22%; bars and wires 19-22%; pipes and extruded shapes 2-3%.

The nomenclature of titanium alloys produced in other capitalist countries (Great Britain, West Germany, France, Japan) is considerably narrower than that of the USA, but the alloys show no fundamental composition differences from those produced in the USA. We might, however, take note of a British alloy of titanium with a small amount of copper (2-3%) and intermetallic-type hardening. It exhibits good technological plasticity in the annealed form and its strength is increased, although not to very high values, after quenching and aging. Copper is also used in the multicomponent alloy Ti-Sn-Cu-Al-Mo.

As compared with unalloyed titanium, the alloys exhibit substantially higher creep resistance owing to the introduction of the alloying additives. In many cases, this property can be improved substantially by heat treatment.

Titanium and its alloys are distinguished by good fatigue strength. On the average, their endurance limits range up to 0.58 of their ultimate strengths. The relationships observed in smooth and notched titanium and titanium-alloy specimens between endurance limit and ultimate strength are similar to the corresponding figures for most structural steels. The endurance limits of titanium alloys, like their other strength properties, rise substantially at very low temperatures (-196°C).

Titanium alloys give poor friction and wear performance. This shortcoming is mitigated by coating the titanium with other metals. Application of a layer of electrolytic nickel has given superior results [38]. The surfaces of titanium products are nitrided for the same purpose.

Phase diagrams of the systems formed by titanium with many of the chemical elements are given in the works of V.N. Yermenko [41] and Ye.K. Molchanova [46].

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alloy  
es:

SYMBOL LIST

| Manu-<br>script<br>page<br>No. | Russian | When<br>typed | Meaning           |
|--------------------------------|---------|---------------|-------------------|
| 30                             | р       | р             | recrystallization |
| 30                             | пх      | м             | melting           |

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## Chapter 4

### CORROSION RESISTANCE OF TITANIUM AND SOME OF ITS ALLOYS

Many Soviet and foreign studies [55-58, 66, and others] have been devoted to the corrosion stability of titanium. We shall therefore set forth briefly below only the basic data on which the applications of titanium and its alloys are based.

Titanium, as a chemical element, is highly active and readily capable of combining with various substances. At the same time, it exhibits good corrosion resistance in many aggressive environments. It is superior in corrosion resistance to stainless steels and other corrosion-resisting materials. The resistance offered by titanium to many aggressive media is comparable to that of platinum under the same conditions.

The basic criterion of a metal's corrosion resistance is its standard electrode potential. The more negative this potential, the lower will be the corrosion resistance of the metal in question. Like aluminum, magnesium, iron, and some other metals, titanium has an irreversible electrode potential. Its theoretical value ranges from -1.21 to -1.30 V for  $\text{Ti}/\text{Ti}^{3+}$ , while direct experiment was indicated values from -0.35 to -0.37 V and even higher. The theoretical standard-potential value gives an idea of the corrosion resistance of titanium under primary ideal conditions that excludes the passivating effect of the environment, which would otherwise result in polarization processes, formation

of protective films, and the other phenomena that accompany electrochemical corrosion.

The stability of titanium in aggressive environments results from the formation of various types of films on its surface. In oxidizing media, the protective film is composed of titanium dioxide. Formation of this film is promoted by nitric acid, chlorine dioxide, cupric chloride, ferric chloride, and sodium hypochlorite. Films with other compositions may be formed in other environments. For example, in hydrofluoric acid or, to a lesser degree, in hydrochloric acid, a film of titanium hydride  $TiH_2$  forms on the surface of the metal.

Titanium alloys are considered stable at corrosion rates up to  $0.05 \text{ g}/(\text{m}^2 \cdot \text{h})$  ( $\sim 0.1 \text{ mm/year}$ ), of reduced stability up to  $0.5 \text{ g}/(\text{m}^2 \cdot \text{h})$  ( $\sim 1 \text{ mm/year}$ ), and unstable up to  $5.0 \text{ g}/(\text{m}^2 \cdot \text{h})$  ( $\sim 10 \text{ mm/year}$ ).

The resistance of titanium to mineral acids varies. It is stable in nitric acid if the surface of the metal is protected from mechanical damage; the stability of titanium in sulfuric, hydrochloric, and phosphoric acids depends on the concentration of the acid and on temperature. The corrosion rates in hydrochloric and phosphoric acids increase with rising acid concentration and temperature; a more complex dependence is observed in sulfuric acid.

Titanium is unstable in hydrofluoric acid, even in the most dilute solutions, owing to the formation of readily soluble complex fluorine compounds. Few organic compounds act on titanium; solutions of oxalic and trichloroacetic acids, in which it is unstable owing to formation of complex compounds, are an exception.

Titanium exhibits high corrosion stability in alkalis, solutions of calcium and sodium hypochlorites, and in moist chlorine. Titanium is characterized by high stability in sea water and in solutions of almost all chlorides at normal and elevated temperatures (except for saturated solutions of aluminum chloride and zinc chloride).

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nitrogen oxides is an exception); no crevice corrosion has been observed in long-term tests.

Titanium also shows no corrosion when placed under stress in many media (exception: fuming nitric acid). Titanium resists cavitation erosion and fatigue corrosion.

The following supplementary remarks may be made in connection with each of the above groups of compounds.

Detailed study of the corrosion rate of titanium in nitric acids of various concentrations has shown that silicon dioxide, which is absorbed by the acid from glass containers, acts as a corrosion inhibitor. It was established from tests in titanium containers that titanium corrodes most rapidly in 40% nitric acid; corrosion increases with rising temperature, to 10 mm/year at 240°C [59]. Cases of explosions during tests of titanium in fuming nitric acid have been reported. Experiments to reproduce such explosions, together with metallographic analyses, indicated that the explosions were caused by grain-boundary precipitation of a dispersed  $\alpha$ -phase, which exhibits pyrophoric properties. It has been reported that fuming nitric acid is explosive in contact with titanium if it contains less than 1.3% of water and more than 6% of  $\text{NO}_2$  [42].

It was established as a result of tests conducted in 99.5%  $\text{HNO}_3$  at 80°C on pipes welded up from various grades of titanium that the stability of the metal is ensured under these conditions if it contains no more than 0.05% each of iron, nickel, and chromium. This figure is considerably smaller than that permitted by the technical specifications applied in the titanium-producing countries. These impurities are stabilizers of  $\beta$ -titanium, which forms on overheating of the weld zones [119].

Titanium remains stable in hydrochloric acid at room temperature only up to a 5% concentration of the acid. When the concentration is raised to 10%, the titanium begins to corrode, and as the acid concentration and temperature are increased further, the corrosion rate rises steadily [58, 60]. The corrosion of titanium in hydrochloric acid is sharply inhibited in the

presence of chlorine [61].

Except for the dilute solutions, titanium exhibits low stability in sulfuric acid. The curve of corrosion rate as a function of acid concentration shows two maxima corresponding to acid concentrations of 40 and 78%, with the corrosion-rate minimum between them corresponding to the 50-65% concentration range. In fuming sulfuric acid, the corrosion rate continues to decrease with increasing content of free  $\text{SO}_3$  up to the 30% point. As the temperature of the sulfuric acid is raised, the corrosion rate of titanium rises sharply, especially in the region of the first maximum, i.e., at a concentration of 40% [58, 62]. The corrosion rate of titanium in sulfuric acid with a concentration of about 100 g/liter increases in the presence of nickel and copper ions [61, page 139].

Like other oxidizing reagents, chlorine inhibits the corrosion of titanium at acid concentrations up to 40% and temperatures to 90°C.

Titanium is extremely stable in ferric-chloride solutions. Characteristically, the addition of ferric chloride to hydrochloric acid sharply inhibits the corrosion of titanium.

Titanium is exceptionally stable in sea water, in which it corrodes at a rate of  $2.5 \cdot 10^{-4}$  mm/year.

Dry gaseous chlorine reacts vigorously with titanium even at 30°C, but corrosion is eliminated in the presence of small amounts of moisture (0.005%). Titanium is not observed to corrode in moist gaseous chlorine (the rate is less than 0.025 mm/year at 100°C).

Minor corrosion damage to titanium is observed in moist gaseous bromine at room temperature. The reaction takes place very slowly in 4% bromine solution: the corrosion rate does not exceed 0.0075 mm/year. Liquid bromine, dry or moist, attacks titanium quickly. The effect of hydrobromic acid is insignificant.

Iodine vapor reacts with titanium at relatively low temperatures (140-150°C). This reaction is the basis of the iodide

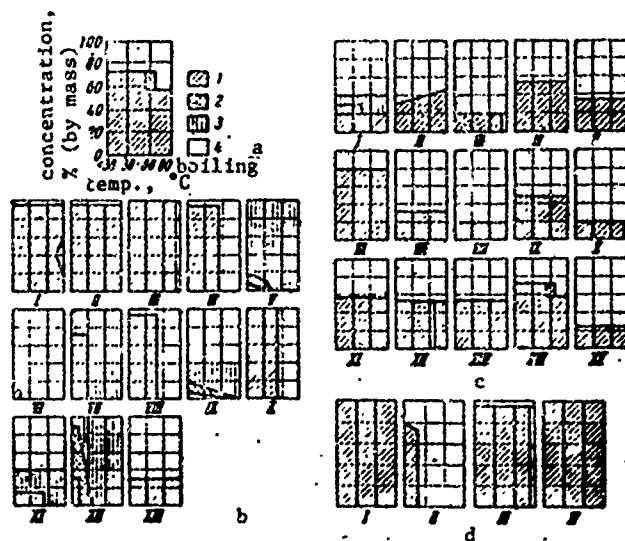


Figure 4. Corrosion of titanium in various environments. a) Key to corrosion diagram: 1) less than 0.13 mm/year; 2) 0.13-0.51 mm/year; 3) more than 0.51 mm/year; 4) corrosion rate not determined or compound decomposes; b) corrosion of titanium in inorganic acids and mixtures thereof; I) nitric acid (aerated); II) nitric acid, un-aerated; III) mixture of nitric and adipic acids (2:1); IV) mixture of nitric and sulfuric acids (10:1); V) sulfuric acid; VI) sulfurous acid; VII) sulfuric acid + cupric sulfate (0.05-1%); VIII) mixture of sulfuric and nitric acids (10:1); IX) hydrochloric acid (aerated); X) mixture of hydrochloric and nitric acids (3:1); XI) hydrochloric acid + cupric sulfate (0.05%); XII) phosphoric acid; XIII) chromic acid; c) corrosion of titanium in alkalis and chlorides: I) aluminum chloride; II) ammonium chloride; III) barium chloride; IV) ferric chloride; V) potassium chloride; VI) calcium chloride; VII) sodium chloride; VIII) nickel chloride; IX) magnesium chloride; X) manganese chloride; XI) cupric (2) chloride; XII) cuprous (1) chloride + dilute hydrochloric acid; XIII) mercuric chloride; XIV) zinc chloride; XV) stannous chloride + stannic chloride; d) corrosion of titanium in gases: I) sulfur dioxide saturated with water vapor; II) hydrogen sulfide saturated with water vapor; III) gaseous chlorine; IV) a mixture of gases: hydrogen, carbon monoxide, and carbon dioxide.

refining process used for titanium. Iodine solutions have no corrosive action on titanium.

Gaseous fluorine reacts with titanium at elevated temperatures, but titanium reacts slowly with anhydrous liquid hydrofluoric acid. Dilute hydrofluoric acid is highly reactive, and the reaction proceeds very vigorously in a 5% solution. Addition of nitric acid retards the corrosion of titanium.

Titanium dissolves not only in hydrofluoric acid, but also in acid media containing the fluorine ion. Since fluorides are easier to handle than hydrofluoric acid, sodium fluoride is introduced into many acid etchants for titanium semifinished products and to etch titanium scrap before regeneration.

Titanium is distinguished by good chemical stability in a number of organic acids. It is not stable in a mixture of glacial acetic acid with acetic anhydride, in tartaric, formic, and especially oxalic acids [61, page 144].

Titanium corrodes very rapidly in dilute sodium chloride in the presence of air; without air, the corrosion is quite insignificant. Titanium oxidizes in the presence of air even under the melt, since oxygen diffuses from the environment through the melt to the metal. An oxide film with the composition  $TiO_{0.2}$  forms on the surface of the metal and then peels off. Corrosion is insignificant in a neutral medium even at temperatures above  $1000^{\circ}C$ .

The corrosion of titanium in fused  $NaCl$  has also been studied in the presence of heavy-metal salts. Salts of copper, nickel, cobalt, cadmium, and iron react with titanium. The titanium surface forms a layer representing the solid solution with the metal of the salt added to the melt (Fe, Ni, Co, Cu, and Cd). This layer breaks up and separates under the action of internal stresses. The corrosion process advances much more rapidly in air than in a neutral medium.

Titanium has satisfactory corrosion resistance in many molten metals. For example, the corrosion is below 0.1 mm/year in sodium at  $600^{\circ}C$ , and between 0.1 and 1 mm/year at  $800^{\circ}C$ ;

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stability is of the same order in bismuth-tin, bismuth-lead, and sodium-potassium alloys and in lithium, magnesium, potassium, and tin (the above data pertain to tests with no oxygen in the gaseous phase above the melt); titanium is unstable in molten zinc.

In contact with many metals, titanium is an efficient cathode and detrimental to them. For example, the corrosion of soft steel, aluminum, gun bronze (88% Cu, 10% Sn, 2% Zn), magnesium, and calcium is accelerated in contact with titanium under exposure to sea water or salt mist. Titanium becomes the anodic component of the galvanic pair in sulfuric acid solutions in contact with aluminum and stainless steel.

Some of the corrosion diagrams given by V.V. Andreyeva and V. I. Kazarin for technical titanium are reproduced in Fig. 4. To amplify on the high activity of titanium at elevated temperatures with respect to oxygen, nitrogen, and hydrogen, we should take note of the metal's ability to react under these conditions with carbon monoxide and dioxide, water vapor, and ammonia. When titanium is heated in air, as before pressworking, water vapor present in the air may decompose on the surface of the titanium and saturate the metal not only with oxygen, but with hydrogen as well. Incandescent titanium can also become saturated with hydrogen in the presence of ammonia or other hydrogen-containing gases present in the furnace atmosphere.

The corrosion stability of the titanium structural alloys whose compositions were given in Table 5 has not been studied as thoroughly as that of technical titanium. However, available data on the stability of OT4 alloy and on VT3-1, VT5, VT5-1, and VT6 permit the inference that their stabilities are quite far below that of technical titanium in a number of aggressive environments, and especially in hydrochloric and sulfuric acids and various organic media. A similar effect is also observed after high-temperature soaking (750-800°C), which is applied before pressworking the metal. The corrosion stability of the specimens dropped markedly, but remain higher in the technical metal than, for example, in OT4 alloy. There are reports [60] to the effect that the corrosion stability of this alloy is the same in many

environments as that of technical titanium. According to foreign data, the alloy Ti-3Al-2.5V has the same stability as technical titanium in hydrochloric and sulfuric acids.

Corr

The corrosion resistance of welded joints in technical titanium and OT4 alloy depends on the type of welding, the structure of the seam metal, and that of the around-the-weld zone. A difference between the corrosion stabilities of the welded joint and the base metal makes its appearance in the aggressive media in which the base metal is in a state of "borderline passivity." This difference is not observed in oxidizing environments - especially oxygen compounds of chlorine - or in nitric acid. Welded joints may be subject to various types of failure in nonoxidizing aggressive media, depending on the composition and nature of the impurities present in them [56].

TABLE 9  
Mechanical Properties of Annealed Corrosion-Resistant Alloys

\*The  
at :

| alloy                      | test temperature, °C             |                                  |              |            |                                  |                                  |              |            | bending angle,<br>degrees |            |     |
|----------------------------|----------------------------------|----------------------------------|--------------|------------|----------------------------------|----------------------------------|--------------|------------|---------------------------|------------|-----|
|                            | 20                               |                                  |              |            | 200                              |                                  |              |            |                           |            |     |
|                            | $\sigma_b$ , kgf/mm <sup>2</sup> | $\sigma_s$ , kgf/mm <sup>2</sup> | $\delta$ , % | $\psi$ , % | $\sigma_b$ , kgf/mm <sup>2</sup> | $\sigma_s$ , kgf/mm <sup>2</sup> | $\delta$ , % | $\psi$ , % | base metal                | seam metal |     |
| unalloyed titanium . . . . | 42                               | 33                               | 22           | 71         | 23                               | 21                               | 12           | 37         | 71                        | 180        | 180 |
| Ti + 10.5% Mo . . . .      | 79                               | 73                               | 19           | 48         | 3                                | 36                               | 36           | 15         | 67                        | 57         | 155 |
| Ti + 30% Mo . . . .        | 79                               | 73                               | 13           | 54         | 3                                | 64                               | 57           | 17         | 63                        | 70         | 163 |
| Ti + 20% Ta . . . .        | 73                               | 68                               | 12           | 55         | —                                | —                                | —            | —          | —                         | —          | —   |
| Ti + 2% Nb . . . .         | 52                               | 45                               | 20           | 73         | 22                               | 26                               | 21           | 26         | 73                        | 180        | 138 |
| Ti + 30% Nb . . . .        | 62                               | 51                               | 20           | 66         | —                                | —                                | —            | —          | —                         | —          | —   |

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Alloyed welding wire with a minimum content of gaseous impurities is used to obtain high-quality seams in welding of titanium alloys.

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The higher corrosion resistance of technical titanium as compared with the structural alloys has made it the material of

TABLE 10  
Corrosion Stability of Annealed Alloys [Test Time  
100 h, corrosion rate in g/(m<sup>2</sup> · h)]

| composition        | material     | test temperature, °C |                                      |                                      |                         |             |
|--------------------|--------------|----------------------|--------------------------------------|--------------------------------------|-------------------------|-------------|
|                    |              | 150                  |                                      |                                      | 200                     |             |
|                    |              | HCl<br>5%            | H <sub>2</sub> SO <sub>4</sub><br>5% | H <sub>2</sub> PO <sub>4</sub><br>5% | HNO <sub>3</sub><br>35% | HCOOH<br>5% |
| unalloyed titanium | sheet        | 120.0                | 90.0                                 | 4.25                                 | 0.934                   | 2.95        |
| Ti+30% Mo          | sheet*       | 0.071                | 0.012                                | —                                    | —                       | 0.0171      |
|                    | welded joint | —                    | 0.002                                | —                                    | —                       | 0.0187      |
| Ti+20% Ta          | sheet        | —                    | 0.000                                | 0.0028                               | 0.0028                  | 0.0018      |
| Ti+2% Nb           | sheet*       | —                    | —                                    | —                                    | 0.0096                  | —           |
|                    | welded joint | —                    | —                                    | —                                    | 0.0061                  | —           |
| Ti+20% Nb          | sheet        | 0.0013               | —                                    | —                                    | —                       | 0.028       |
| Ti+0.2% Pd         | bar          | —                    | 0.000                                | —                                    | —                       | 0.0005      |

\*The weld seam was run crosswise through the test plate at its center.

TABLE 11  
Stability of Titanium Alloyed with Palladium (0.2%) as  
Compared with Technical Titanium

| environment   | test conditions         | corrosion, mm/year |       |
|---|-------------------------|--------------------|-------|
|   |                         | alloy<br>Ti+0.2%Pd | Ti    |
| HCl, 10%<br>HCl, 25%<br>HCOOH, 50%  | boiling                 | 0.025              | 0.366 |
|   |                         | 0.085              | 31.0  |
|   |                         | 0.576              | 3.64  |
| HCl, 10%<br>HCl, 15%<br>H <sub>2</sub> SO <sub>4</sub> , 5%<br>H <sub>2</sub> SO <sub>4</sub> , 10% | 70°C, air<br>saturation | 0.061              | 7.37  |
|   |                         | 0.162              | 17.05 |
|   |                         | 0.676              | 7.21  |
|   |                         | 0.102              | 14.22 |

preference in chemical engineering. However, further study of the properties of titanium alloys has shown that there is a possibility of improving the corrosion resistance of titanium substantially by alloying it without detriment to the attractive mechanical properties of the alloys or the highly important weldability

property.

Alloying elements that raise the corrosion stability of titanium include molybdenum, tantalum, zirconium, niobium, and the noble metals.

When titanium is alloyed with molybdenum, especially at 30% Mo, the corrosion stability of the titanium alloys in hydrochloric, phosphoric, and sulfuric acids rises sharply. Alloying of titanium with niobium (30%) raises the corrosion stability of titanium alloys in hydrochloric acid. Alloys with niobium are unstable in sulfuric and phosphoric acids at 150°C. Alloys of titanium with zirconium (up to 15%) and tantalum (to 20%) are stable in phosphoric acid. Alloying with these metals does not improve the stability of titanium in hydrochloric and sulfuric acids.

The introduction of palladium or platinum, even in small quantities (no more than 0.1-0.2%) sharply increases the corrosion stability of titanium alloys in solutions of hydrochloric and sulfuric acids at concentrations up to 30% and temperatures to 100°C. Alloying with tin and rhenium has not produced good results.

Corrosion-resistant titanium-based alloys with the following compositions have been developed: Ti + 18.5% Mo; Ti + 30% Mo; Ti + 20% Ta; Ti + 2% Nb; Ti + 30% Nb; Ti + 0.2% Pd.

The mechanical properties of these alloys are listed in Table 9, and corrosion-resistance figures in Table 10 [57]. The alloys of the compositions listed in Table 9 can be deformed and argon-shielded-arc-welded with good results.

Data on the stability of titanium alloyed with palladium (0.2%) are given in Table 11 for comparison with technical titanium [63].

Work has begun to investigate the corrosion stability of ternary alloys. It has been shown that alloys of titanium with palladium are improved by the introduction of chromium, molybdenum, or zirconium; the stability of the titanium-molybdenum

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alloy is improved by addition of 5% Cr [58].

The general relationships encountered in this question are as follows. The anodic activity of titanium can be lowered and its capacity for passivation increased by alloying with: a) noble metals (Pd, Pt, and others), which shift the standard potential in the positive direction; b) elements that raise the thermodynamic stability of the alloy (Ni, Mo); c) elements that enhance the tendency of titanium to passivation (Cr, Zr, Ta, Nb, V) [58].

The corrosion resistance of titanium and its alloys can be improved by anodizing and by the use of galvanic coatings. It has been reported that the corrosion resistance of titanium alloys such as OT4 and VT5-1, in 20% sulfuric acid can be improved substantially by holding the finished product in air at 750-850°C for 3-5 h. Saturation of the surface layer with oxygen to a depth of 0.1-0.3 mm passivates it [64].

Before anodizing, the titanium surface is degreased and pickled in an aqueous solution of a mixture of 1.5% HF and 20% HNO<sub>3</sub>. Anodizing can be done in various electrolytes, e.g., 20% sulfuric acid. Anodizing substantially improves the corrosion stability of titanium and its alloys in sulfuric and phosphoric acids, alcoholic bromine, and other aggressive environments.

Application of galvanic coatings to titanium involves certain difficulties - it is first necessary to treat the piece to remove the oxide film and form a film of titanium hydride. Chromium, nickel, silver, copper, cadmium, and other metal platings are applied to titanium [38, 65].

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Chapter 5

APPLICATIONS OF TITANIUM

The possibilities for extensive use of titanium alloys as structural materials for various purposes stem from the singular properties that distinguish titanium and its alloys from other materials.

TABLE 12  
Breakdown of Titanium Consumption in the USA

| field of application             | 1963   | 1964 | 1965 | 1966  | 1970* |
|----------------------------------|--|------|------|-------|-------|
|                                  | breakdown of titanium consumption, %, for the following total tonnages of semifinished products consumed |      |      |       |       |
|                                  | 5500   | 7000 | 8400 | 12500 | 19000 |
| jet engines                      | 23   | 24   | 42   | 47    | 25-30 |
| military aircraft                | 29   | 30   | 30   | 28    |       |
| rockets                          | 22   | 21   | 15   | 15    | 20-15 |
| civil aviation                   | 9  | 8    | 13   | 10    | 30-30 |
| misc., including chemical equip. | 7  | 8    |      |       | 22-25 |

\*Estimated.

The literature on the problems of using titanium is quite voluminous and is being added to continuously. In contrast to foreign reports and papers, which pertain to the use of titanium in some narrow field, the Soviet literature has offered monographs that examine the problems of using titanium in specific fields of mechanical engineering in minute detail, setting forth recommendations for the machining of titanium, its welding, etc. [38, 39, 55, 56, 56, 66, 67]. The detailed survey [68], which is descriptive in nature, should be cited among the foreign sources on this problem.

The consumption of titanium in various industrial branches in the USA during recent years is characterized by Table 12 [121-124], which also gives projected estimates.

It follows from the data in Table 12 that, despite the substantial increase in the civilian uses of titanium, the industrial branches servicing the military will remain the basic users of titanium for a long time to come [76].

In military aircraft construction, titanium is used preferentially for the manufacture of engine components (80-90%) - for flame tubes and exhaust nozzles, combustion-chamber housings, turbine hoods and rotors. The limited use of titanium in the fabrication of airframe components (10-20%) has apparently been due to the inadequate hot strength of titanium alloys. In 1966, this figure reached 30% as a result of the development of new alloys.

It appears that titanium alloys will be used more extensively for the skins of supersonic aircraft as their hot strength is improved. It is projected that 60-90% of the structures used in aircraft capable of Mach 2.5-3 will be made from titanium alloys [77, 78]. It has been reported that the firm TMCA has produced a new alloy designated Ti679, which contains silicides, for the manufacture of jet-engine parts. According to a statement from the firm, use of this alloy makes it possible to raise the running temperatures of the engine parts from 400 to 480°C [79]. Work to improve the hot strength of titanium alloys is being pushed in this context [78, 79].

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It has been reported [69] that substitution of titanium engine parts for steel ones has produced the following weight savings: exhaust pipes 32%, engine coverings 39%, bulkheads and nacelles 25%. In stressed elements, the weight savings is in many cases even greater, since titanium has a higher specific strength than steel. For example, the weight savings is 32-41% for engine compressor vanes and 38-67% for compressor disks. Many fastening components for aircraft are made from titanium. Substitution of titanium for steel in these components may yield weight savings up to 42%. As we know, a 1-kg engine-weight reduction makes it possible to save up to 10 kg of total aircraft mass by lightening the fuselage.

Use of titanium alloys made it possible to reduce the mass of the DC-8 airliner by 430 kg. This saves \$2.6 million over 7 years of operation of the airplane [80]. In the XB-70A supersonic airplane, which weighs 58 tons, 22 thousand parts weighing 5.4 tons are made from titanium alloys [78].

The effectiveness of using titanium in jet-engine parts in motion at high temperatures is characterized by the following comparative figures: the compressor rotor of a jet engine failed at 20 thousand rev/min when it was made from aluminum (mass 11 kg), at 17 thousand rev/min when it was made from steel (mass 14 kg), and at 25 thousand rev/min when it was made from titanium (mass 8 kg) [70].

In civil aircraft construction, as in the military, titanium is still used for the most part to make engine components and the wheels of the aircraft, which last several times longer than conventional wheels [71, 81].

In rocket engineering, most of the titanium (more than 80%) is used to make compressed-gas tanks, casings for solid rocket engines, and liquid-hydrogen tanks. Titanium is also a basic structural material for spacecraft. Although titanium rocket parts now cost 20-25% more than the corresponding steel components, the weight savings ranges above 40% [116].

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Prospects for the use of titanium alloys in submarine hulls have improved with mastery of welding techniques for thick titanium sheets, although this application has accounted for only 1% of the titanium used in recent years. The properties of titanium that make it attractive for use in this field are its high specific strength, excellent corrosion stability in sea water, and its low density, which makes it possible for the craft to dive considerably deeper than steel submarines [72, 78]. Titanium and its alloys are used in shipbuilding to make many components that must resist exposure to sea water and other aggressive environments, e.g., to make diesel-engine mufflers, condensers and heat exchangers, measuring instruments, radars, and marine-engine parts.

Titanium has been tested successfully in the manufacture of parts for recoilless weapons. One weapon took 36 kg of titanium, and the entire run about 1 thousand tons. Titanium is of particular interest in that it enables us to lighten weapons that are to be hand-carried or ferried by air. For example, a titanium mortar baseplate weighs 11 kg as compared to 22 kg when steel is used. Use of titanium in the production of artillery weapons makes it possible to secure high maneuverability and long service life [68].

It is estimated that the use of titanium for tank armor plates will reduce their weight by about 25%.

The foreign literature, and American sources in particular, devote most of their attention to the use of titanium in chemical engineering, which is highly promising even at the present cost level of titanium semifinished products.

As a prime example of chemical machinery that can be made from titanium on an industrial scale, mention must be made of the heat exchanger, which, along with its corrosion resistance, has two additional important advantages. Titanium is not wetted as well by liquids as are copper, stainless steel, and the alloy Hastelloy C. The result is that on condensation in titanium condensers, many liquids form individual drops, which quickly run

off the surface, instead of films [82]. The other property of titanium is that an oxide film forms on its surface and facilitates removal of sediment from the heat-exchanger surfaces. As a result, a high heat-transfer coefficient is preserved throughout the entire operating life of the heat exchanger [83]. Substitution of titanium for lead coils made it possible to reduce their length to one-fifth and their diameter by half [84]. In another case, the higher cost of installing titanium coils was covered in 1.5 years [85].

In view of its high specific strength, titanium has been used to make rotors for high-speed centrifuges, for which lower weights of the rotating elements are particularly important.

Titanium is used to make the vanes and housings of centrifugal pumps used to transfer solutions of chlorides, dilute hydrochloric acid, and various organic acids. In many cases, such pumps work for years, while pumps made from nickel-chromium-molybdenum steels fail after a few months [39]. The service lives of titanium injectors are correspondingly longer than those of iron types.

In the last analysis, the basic factor responsible for the use of titanium in various nonmilitary branches of mechanical engineering has been its cost effectiveness, which depends to a substantial degree on the corrosion stability of titanium under the particular set of conditions, and on cost in those cases in which corrosion stability is not a major consideration.

The high cost of titanium has stimulated research to develop a technology for titanium-facing of steels to be used in the manufacture of chemical apparatus [68, 72, 86-88]. One of the simplest methods of cladding titanium, which is already in industrial use, employs an explosive wave to produce a bimetal. However, metal cladded without an intermediate layer cannot be heated above 500°C, since a brittle interlayer forms at higher temperatures as a result of mutual diffusion of the metals [89]. Production of steel pipes 25 mm in diameter with internal titanium linings has been set up [90].

It will be interesting to compare cost calculations for an autoclave 1.8 m long and 0.76 m in diameter with hemispherical bases when it is made from various materials [91]:

|   | Relative material cost | Relative cost of autoclave |
|---|------------------------|----------------------------|
| Stainless steel 316, thickness 3 mm.....    | 1.00                   | 1.00                       |
| Titanium.....                               | 5.00                   | 3.30                       |
| Titanium-clad carbon steel (61 + 2 mm)..... | 1.12                   | 1.56                       |

Use of titanium is advantageous in spite of this equipment-cost ratio, since its stability in many aggressive environments is several times better than those of high-alloy steels and other materials. Thus, a stainless-steel autoclave was replaced by a titanium unit that cost 2.2 times as much. However, the service life of the titanium autoclave was found to be 5-6 times longer. Titanium coils were found effective even when substituted for plain steel coils. The titanium coils were 3.8 times more expensive, but it was found that they were practically immune to wear; the steel coils, on the other hand, lasted from 9 to 12 months [87]. A titanium drum filter for separation of zirconium sulfate costs about twice as much as a rubber-faced steel drum. This premium was covered in two years by the reduction in outlay for repairs on the steel filter and its replacement, when worn, by a new filter of the same kind [92]. Titanium equipment is effective not only in virtue of its higher stability. Replacement of titanium for steel apparatus made it possible to raise the temperature of a reaction in which a material was decomposed in nitric acid from 77 to 150°C, with increased extraction [87, 115]. The examples cited above are based on the current cost of titanium and semifinished titanium products. It is predicted [93] that by 1970, technological improvements in the acquisition and processing of titanium will have reduced the cost penalty incurred in using titanium equipment instead of steel. For example, introduction of a technology for the fabrication of welded titanium pipes lowered their cost by about half as compared with the

cost of seamless pipes; the minimum pipe wall thickness was reduced from 1.6 to 0.9 mm.

Manufacture of large chemical equipments would be impossible without appropriate advances in the welding of titanium. Without going into details, we may note that one solution to this problem involves doing the welding inside inert-gas-filled polyethylene bottles. Fabrication of liquid-hydrogen tanks 7 meters long and 2.5 m in diameter by this method has been reported [94]. Inert-gas-filled plastic bags are also used to weld small parts.

The USSR has developed a technology of submerged-arc titanium welding that makes it possible to join pieces of practically any thickness [95]. A literature report [96] tells of the development of a technology for welding very thin titanium parts to very thick ones, e.g., thin-walled pipes to valves.

Master of technologies for the casting of titanium, and especially of parts for equipment and fittings that are now made by welding, will help expand the range of application of titanium. This will require development of appropriate furnace designs and selection of mold materials that will not interact with titanium. Until recently, graphite molds have been used, at the cost of a certain amount of carburization of the surface layer of the casting. However, graphite molds survive only a single casting operation. Use of a special graphite increased mold service life to 10-12 castings, but this was still inadequate and increased the cost of the process considerably. It is reported that the American firm TMCA has found a new mold material that permits up to one hundred castings in a single mold [97]. Cast titanium and titanium-alloy components are even now being used successfully as replacements for forged and welded pieces. The largest cast titanium products now being produced weigh about 180 kg, are 1.8 m long and 0.9 m wide; the minimum casting wall thickness is 2.4 mm. It is predicted that improvements to titanium casting technology will help substantially in broadening the nomenclature of cast products and lowering their cost [98].

Broad-scale research in the USSR has resulted in the development of a technology and equipment for production of titanium

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castings [99]. For example, high-capacity smelting-and-teeming furnaces have been designed, and research is being done to find the most suitable materials for moldmaking.

Turning to industrial chemical processes, where titanium has already secured a foothold, we should first make mention of the production of chlorine. The stability of titanium in moist chlorine had led to its use in the fabrication of heat exchangers. Although the cost of 1 m<sup>2</sup> of titanium heat exchanger is 1.86 times that for a graphite exchanger, the area of the exchanger can be reduced by a factor of 1.8 because of the high heat-transfer coefficient of titanium. The service life of a titanium condenser is 5 times that of a graphite unit. As a result, installation of titanium condensers has been to considerable economic advantage [83].

Titanium pumps for transfer of hot nitric acid or heated chloride and salt solutions last 10-20 times as long as similar stainless-steel pumps [76]; this more than offsets the higher first cost of the titanium pumps.

Since titanium presents an explosion hazard in contact with fuming nitric acid, it is used to make equipment to hold nitric acid at concentrations no greater than 60-70% [42, 43, 87].

Platinized titanium anodes are being used successfully in mercury and diaphragm-type electrolyzers for chlorine production instead of anodes made from graphite, ferrosilicon, and other materials. The stability of the titanium anodes ensures that the interelectrode distance will remain constant, i.e., it maintains stable operating conditions, increases productivity, and lowers operating costs [100]. A great advantage is that the platinum coating need not be continuous; it can be applied only to specific zones of the anode or have porosity [101]. Four foreign firms have concluded an agreement on the use of platinized titanium anodes for the production of chlorine [102]. Such anodes are also used in the production of perchlorates, for cathodic corrosion protection, especially in sea water, and in the electrolytic production of gold, platinum, rhodium, silver, chromium, nickel, and other metals and organic compounds [103].

Chlorine-handling pipes are made from titanium. Because of the absence of corrosion, the 356-mm-diameter pipelines have thin walls ranging from 0.8 to 1.3 mm.

In addition to the chlorine industry, titanium is coming to be used successfully in the cellulose-and-paper industry, for example in the production of calcium hypochlorite, sodium chlorate, and soda.

Among the organic-chemical processes, note should be taken of the production of acetic acid and the dyes made with it and with formic and other organic acids; the production of urea from carbon dioxide and ammonia; processing of coke-chemistry products (dilute sulfuric acid solutions containing  $H_2S$ ,  $HCN$ ,  $SO_2$ , and organic compounds); petrochemistry and the production of synthetic fibers.

Titanium is used in building equipment for dye production where the conditions of the process require high purity of the final product, as well as apparatus for the actual dyeing process [66, 104-106].

An acetaldehyde plant equipped with apparatus surfaced with titanium was placed in operation in 1962 at Bay City, Texas. The total faced area is  $2140 m^2$ . The largest piece of equipment is 9.75 m long and 3.04 m in diameter [107].

In 1963, titanium was first put to use in the production of desalinating equipment - a highly promising field of application for the metal. The first such unit used 155 km of titanium tubing [108]. Development of a low-cost technology for manufacture of titanium pipes by welding will promote their application. The firm TMCA has developed a special machine for production of such pipes [76].

Titanium equipment has come into extensive use in the USSR and abroad in a number of hydrometallurgical processes - in the processes in which the raw material is prepared for extraction of titanium and molybdenum (dilute hydrochloric acid solutions, solutions containing sulfur compounds), in the production of nickel (acidic solutions containing Ni, Cu, Fe, Co and Cl ions) [39,

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101, 109]. For example, it has been established that titanium flow-control fittings last 5-10 times longer than those used earlier, which were faced with rubber, faolite, and other protective coatings [110].

Cathodes made from an alloy of titanium with palladium (0.1%) are used on an industrial scale in the production of manganese. It has been found that these cathodes have a secondary advantage: weak adhesion of the manganese deposit to them [71]. Titanium cathodes behave similarly in the electrolytic production of nickel [109].

Titanium has come into extensive use in electroplating, where it is used to make baskets in which soluble anodes are placed. This ensures full utilization of the anodes [111]. Titanium is also used to make hooks and hangers for products to be immersed in galvanic baths [112].

Among the fields where the use of titanium does not involve large amounts but is nevertheless advantageous, we should take note of medicine -- the manufacture of medical instruments and internal prostheses. It has been established that the presence of titanium in the organism is quite innocuous, and that bones and muscle tissue concrese with it. Getters for the maintenance of ultrahard vacuums represent another field of application of titanium.

Railway and automotive transportation is a promising field of application of titanium. The economic advantages will be reflected here in lowered fuel consumption and increased cargo-carrying capacity. However, these possibilities will be realized only when the cost of semifinished titanium products is reduced to about half of the 1965 level, i.e., to \$4-6 per kilogram and when the technology of casting titanium has been assimilated. The potential use of titanium by the American automotive industry has been estimated at 16 thousand tons annually [93]. At the present time, only experimental racing-car bodies are being made of titanium.

Manufacture of steam and gas turbines also represents a promising field for the use of titanium.

According to predictions compiled by the Battelle Institute in 1962, the annual use of titanium semifinished products in the USA was to be 23 thousand tons in 1970 (including 2.5-5.0 thousand tons in the chemical-equipment industry) [73].

Considering the data given previously (see page 7) on the expected increase in titanium-sponge production by 1970, as well as the rapid increase in the consumption of titanium semifinished products (see Table 12), we may conclude that these predictions are realistic.

According to British sources, the total production of titanium semifinished products in capitalist countries will be 16 thousand tons by 1970 [113] and 35 thousand tons by 1975 [19].

It has been predicted that by 1970, the maximum strength of deformable titanium alloys will have reached 180 kgf/mm<sup>2</sup>, and that of the foundry alloys to 155 kgf/mm<sup>2</sup>; their service temperatures will be approaching 600°C.

It appears that the basic mass of the titanium produced in years to come will be used in space engineering, since the use of titanium in this field is expanding more rapidly than it is in aviation. A large amount of titanium will obviously go into the manufacture of hulls for deep-water submarines. Extensive use of titanium in weapons production may be expected only if its cost is reduced substantially [114].

In conclusion, we should study predictions regarding the scale of titanium consumption on the basis of the projected cost of semifinished products. At a semifinished cost of \$4.4-6.6 per kilogram (at the end of 1964, the average prices of titanium semifinished products were as follows, in dollars/kilogram: sheet and ribbon 11.0; plates 8.6; wire 8.0; forging blanks 5.4; hot-rolled bars 7.1 [22]), the consumption of titanium may rise in capitalist countries to 56-80 thousand tons per year, including 18-27 thousand tons for military aircraft construction, 1.8-2.7 thousand tons for civil aircraft construction, 13.5-18 thousand tons for

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machinery (including chemical), 1-2 thousand tons for shipbuilding, 7.2-9 thousand tons for weapons production, 11-16 thousand tons for motor vehicles, 1-2 thousand tons for railway transport, and 2.7-3.6 thousand tons for miscellaneous uses. If, on the other hand, the cost of semifinished products drops to 2.2-3.3 dollars/kg, the annual consumption of titanium may be expected to reach 200-270 thousand tons [113].

To cut the cost of titanium semifinished products appreciably, it will be necessary to improve the technology by which titanium tetrachloride and titanium sponge are produced and refined. Important steps on the road to this goal will be the development of a continuous titanium-extraction process, improved production of titanium castings, rational utilization of all titanium scrap, development and introduction of secondary titanium alloys, etc.

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Part II

TITANIUM RAW MATERIALS AND THEIR  
PREPARATION FOR CHLORINATION

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## Chapter 6

### TITANIUM MINERALS AND ORES AND THEIR CONCENTRATION

Titanium is one of the most widely distributed elements. The earth's crust contains 0.61% (by mass) of Ti, or about 1% when converted to  $TiO_2$  [1, 2]

No fewer than 60 titanium-containing minerals are known. Titanium occurs in various quantities in many rock-forming minerals - pyroxenes, amphiboles, micas, garnets, etc. [1-8].

Titanium is present in the quadrivalent form in practically all minerals. Ilmenite ( $FeO \cdot TiO_2$ ) is the most common of all titanium minerals. The small ionic radius of titanium (0.64 Å) results in the formation of stable natural oxides. The most stable titanium mineral, rutile ( $TiO_2$ ), has a tetragonal crystal lattice. Its polymorphic modifications (anatase and brookite, as well as leucoxene, an alteration product of ilmenite) are less stable, and are transformed under environmental effects into the more stable form in the sequence: leucoxene + anatase + brookite + rutile.

Table 13 lists the most important titanium minerals, which can be broken down into 5 characteristic groups: the rutile, ilmenite, perovskite, niobotantalotitanate, and sphene groups [2, 5, 7]. Rutile is encountered comparatively rarely in nature as a monomineral. Usually, metals with similar ionic radii are included isomorphically in its crystal lattice: e.g.,  $Fe^{2+}$  (0.83 Å),

TABLE 13  
The Most Important Titanium Minerals

| mineral                     | chemical formula  | TiO <sub>2</sub> content in mineral, % | density, g/cm <sup>3</sup> |
|-----------------------------|---|--|----------------------------|
| rutile group                |   |  |                            |
| rutile . . . . .            | TiO <sub>2</sub>  | 90-98                                  | 4.23(4.18-5.2)             |
| anatase . . . . .           | TiO <sub>2</sub>  | 90-100                                 | 3.8-3.9                    |
| brookite . . . . .          | TiO <sub>2</sub>  | 90-100                                 | 3.9-4.2                    |
| ilmenorutile . . . . .      | (TiNb, Fe <sup>3+</sup> )O <sub>2</sub>   |  |                            |
| struverite . . . . .        | (Ti, Ta, Fe <sup>3+</sup> )O <sub>2</sub>   |  |                            |
| leucokoen . . . . .         | TiO <sub>2</sub> · nH <sub>2</sub> O  | 80-85                                  | 3.7-4.1                    |
| xantitan . . . . .          | TiO <sub>2</sub> (AlO <sub>2</sub> ) · nH <sub>2</sub> O                                |  |                            |
| nigrine . . . . .           | (Ti, Fe)O <sub>2</sub>  |  |                            |
| chromorutile . . . . .      | (Ti, Cr)O <sub>2</sub>  |  |                            |
| ilmenite group              |   |  |                            |
| ilmenite . . . . .          | FeTiO <sub>3</sub> or (FeO · TiO <sub>2</sub> )   | 31.8                                   | 4.5-5                      |
| geikielite . . . . .        | MgTiO <sub>3</sub>  | 67-68                                  | 4.0                        |
| manganoilmenite . . . . .   | (FeMn)TiO <sub>3</sub>  |  |                            |
| pyrophanite . . . . .       | MnTiO <sub>3</sub>  |  | 4.88                       |
| titanomagnetite . . . . .   | FeTiO <sub>3</sub> · Fe <sub>3</sub> O <sub>4</sub>                                     |  |                            |
| hematite-ilmenite . . . . . | FeTiO <sub>3</sub> · Fe <sub>2</sub> O <sub>3</sub>                                     |  |                            |
| senaitite . . . . .         | (Fe, Mn, Pb)TiO <sub>3</sub>  | 57-58                                  |                            |
| arizonite . . . . .         | Fe <sub>2</sub> O <sub>3</sub> · 3TiO <sub>2</sub>                                      | 80-82                                  | 4.25                       |
| pseudobrookite . . . . .    | Fe <sub>2</sub> O <sub>3</sub> · TiO <sub>2</sub>                                       | 44-53                                  | 4.8                        |
| hegbaumite . . . . .        | 3MgAl <sub>2</sub> O <sub>4</sub> · Fe <sub>2</sub> O <sub>3</sub> · MgTiO <sub>3</sub> |  | 3.81                       |
| perovskite group            |   |  |                            |
| perovskite . . . . .        | CaTiO <sub>3</sub>  | 28.4                                   | 4.1                        |
| knopite . . . . .           | (Ca, Ce)(Ti, Fe)O <sub>3</sub>  |  | 4.21                       |
| dysanallyte . . . . .       | (Ba, Ca, Na)(Ti, Fe, Nb)O <sub>3</sub>  |  |                            |
| uhligite . . . . .          | Ca(Ti, Al, Zr, Ce)O <sub>3</sub>  |  | 4.15                       |
| lopatite . . . . .          | (Na, Ca, Ce)(Nb, Ta, Ti)O <sub>3</sub>  | 28                                     | 4.75-4.88                  |
| niobotantalotitanate group  |   |  |                            |
| pyrochlore . . . . .        | (Nb, Ca . . . . .)(Nb, Ti, Ca, F, Cl) <sub>2</sub> O <sub>7</sub>                       |  | 4.2-6.4                    |
| microlite . . . . .         | (Nb, Ca . . . . .)(Ta, Ti, Ca, F, Cl) <sub>2</sub> O <sub>7</sub>                       |  |                            |
| sphene group                |   |  |                            |
| sphene . . . . .            | CaTi(SiO <sub>3</sub> )O  | 40.8                                   | 3.4-3.88                   |
| yttrotitanite . . . . .     | (Ca, Y, Ce)Ti, Al, Fe(SiO <sub>3</sub> )O   |  |                            |
| surmanite . . . . .         | Nb, Ti(SiO <sub>3</sub> ) <sub>2</sub> (OH) · H <sub>2</sub> O                          |  | 3.13-2.64                  |
| fermanite . . . . .         | (Ca, Na)(Ti, Nb)X <sub>2</sub> (SiO <sub>3</sub> ) <sub>2</sub> (OH, F) <sub>2</sub>    |  | 3.44                       |

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Nb<sup>5+</sup> (0.69 Å), Ta<sup>5+</sup> (0.69 Å), tin, vanadium, chromium, solid solutions of hematite and ilmenite, etc. Rutile segregations are encountered in places together with other stable minerals.

Anatase is the last stable polymorphic modification of titanium dioxide, and is usually encountered together with rutile in sedimentary rocks, clays, and especially in bauxites.

Brookite is seldom encountered in nature, and is usually found together with rutile and anatase. Brookite is transformed to rutile at temperature above 1040°C.

Leucoxene is formed under natural conditions as a result of oxidation of ilmenite or other titanium minerals. The leucoxenization process may continue until titanium dioxide is formed.

Ilmenorutile is rarely encountered in nature. Isomorphic impurities are usually present in it: FeO (up to 12.3%), Nb<sub>2</sub>O<sub>5</sub> (up to 32%), and Ta<sub>2</sub>O<sub>5</sub> (up to 14.7%).

Straverite is similar to ilmenorutile, but contains somewhat larger amounts of tantalum. It is rarely encountered in nature in the free form.

All minerals of the ilmenite group (except titanomagnetite and hematilmenite) are double oxides of the type RORO<sub>2</sub> that crystallize in the corundum lattice. Ilmenite is sometimes called crichtonite or titanium ironstone.

Titanomagnetite, a solid solution with various proportions of ilmenite and magnetite, and hematilmenite, a solid solution of ilmenite and hematite, are encountered most frequently in rocks. Ilmenite is formed by the interaction of titanium dioxide with ferrous oxide in much the same way as the higher and lower oxides of iron form magnetite. During the slow solidification of the magma deep in the earth's crust, during which di- and trivalent iron and quadrivalent titanium accumulate in the residual melt, ilmenite and magnetite crystallize out into individualized granules, forming a mechanical mixture. Thus, titanomagnetite and hematilmenite can be classified in the ilmenite group only conditionally. The presence of individual ilmenite and magnetite

grains makes it possible to separate these minerals by mechanical concentration methods.

Under certain conditions, ilmenite is subject to one or another degree of leucoxenization, and leucoxene fringes may be observed on its granules.

As we noted above, the leucoxinization process may continue to the formation of rutile, which retains the external form of the ilmenite.

At high temperatures in a hydrothermal and oxidizing environment, the ilmenite lattice is reconstructed and pseudobrookite is formed; the next stage is the formation of arizonite and leucoxene. All of the other minerals - geikielite, negbaumite, pyrophanite, and senaite - are seldom encountered in nature, and usually occur as impurities in various minerals.

Perovskite is similar to the ilmenite-group minerals, but the larger ionic radius of calcium causes it to crystallize in a cubic lattice. The titanium can also be replaced by isomorphic materials in this group of minerals. Depending on the composition of the isomorphic impurities, perovskite is sometimes known as knopite or dysanalyte.

Loparite is a common rock-forming mineral encountered in alkaline rocks. Its composition is complex and inconstant. A characteristic loparite composition is (in %): 39.2  $TiO_2$ , 11  $Nb_2O_5$  +  $Ta_2O_5$ ; 16-19  $Ce_2O_3$ ; 4.2-5.2  $CaO$ ; 7.8-9  $Na_2O$ ; 0.2-0.7  $K_2O$ ; 0.5-0.6  $ThO_2$ ; 0.03-0.05  $U$ ; 0.2-0.7  $SiO_2$ ; and 3.5  $H_2O$  [7].

The minerals of the niobotantalotitanate group crystallize in the cubic lattice. These minerals are richer in the rare elements, but they have no independent industrial importance for the production of titanium at the present time owing to the small titanium contents in the ore.

Sphene is a rather common mineral. It is encountered in nature in the form of scattered inclusions in granites, diorites, etc. Large concentrations of sphene - reserves ranging into the tens of thousands of tons - are encountered in pegmatites and pegmatoid nephelinic syenites. On subjection to hydrothermal

conditions, sphene decomposes with formation of rutile or anatase. Quite frequently, it contains up to 6% of ferrous oxide, up to 3% of manganous oxide, along with magnesium oxide, ferric oxide, alumina, and the like.

The varieties of sphene - yttrotitanite, murmanite, and fersmanite - are very rare minerals.

The minerals given in Table 13 may be encountered in various quantities in titanium ores. However, rutile and ilmenite are of the greatest importance for acquisition of metallic titanium and pigment titanium dioxide. Ilmenite deposits are so widely distributed and large as to permit large-scale development of the titanium industry.

#### Titanium Ores

The titanium ores that are significant for industrial production can be broken down for convenience into two types: native ilmenite-titanium-magnetite and alluvial rutile-ilmenite-zirconic ores.

The native titanium-magnetite ores of the USSR include those of the Kusa, Kopan, Kachkanar, and other deposits [5-7]. The reserves of native titanium ores in the Urals run to many millions of tons. This ore type also includes the ores of the Piney River, McIntyre, Tejavics, and Roseland deposits in the USA, those of Otonmaki in Finland, and others. The loparites, which contain niobium, tantalum, and other rare elements in addition to titanium in the form of perovskite and titanomagnetite, are an example of composite native ores [8, 9].

The ores of the Kusa deposit are typical ilmenite-magnetite ores and are confined to gabbrocrystalline rocks. The continuous ore bodies of this deposit are arranged in parallel vein-ore lens, shaped beds. Magnetite and ilmenite, of which the magnetite represents about 60-70%, account for 90-95% by volume of these ores. The magnetite grain size range is 0.06-1.0 mm (average 0.2-0.3 mm). The secondary ore minerals here are hematite, leucoxene, rutile, pyrite, and chalcopyrite. The nonmetallic minerals encountered include chlorite, hornblende, resorbed plagioclase, garnet,

epidote, biotite, calcite, breunerite, and others. The average percentage contents of the components in Kusa ore, in %, are 53 Fe (including 27.6 FeO and 48.2 Fe<sub>2</sub>O<sub>3</sub>); 14.21 TiO<sub>2</sub>, 0.65 V<sub>2</sub>O<sub>5</sub>; 0.122 S; 0.01 P; 3.18 SiO<sub>2</sub>; 2.98 Al<sub>2</sub>O<sub>3</sub>; 0.67 Cr<sub>2</sub>O<sub>3</sub>; 3.33 CaO; 0.50 MnO; 0.005 MgO; 0.12 K<sub>2</sub>O; and Na<sub>2</sub>O; 0.25 H<sub>2</sub>O.

The ores of the Chernorech'ye, Nedvedevka, Lopan, Ivanov, Matkal'sk, and other deposits in the USSR are similar in composition and ore-body characteristics to the ores of the Kusa deposit.

In Quebec province in Canada, the most massive native deposit of hematite-ilmenite ores is being worked at Lac Thiault in the Allard Lake region. The total reserves of ores in this region are estimated at 150 million tons, including 125 million tons at Lac Thiault. The main ore body is 1080-920 m across and the thickness of the sheet exceeds 90 m in some locations. The ores of this deposit contain about 75% ilmenite, 20% hematite, and 5% other minerals. The TiO<sub>2</sub> content varies in the range from 32 to 36%. The Lac Thiault deposit is the raw-material base for a mill at Sorel, at which slags with a high titanium content are smelted out.

Alluvial titanium deposits were formed under the influence of exogenous rock-destruction processes. Those minerals in these rocks that resisted chemical alteration accumulated in the sandy fraction of the weathering crust, while the unstable minerals were carried away from the deposit. Ilmenite is one of the minerals that are stable under these conditions. However, even it is subject to leucoxenization. Ilmenite, rutile, zircon, and other heavy minerals are carried out into the ocean by rivers and deposited in the sand along the coast. This natural concentration is accompanied by hydrodynamic density and size grading of the sand, with the ultimate result the formation of large deposits of titanium-zirconium ores.

Typical placer deposits are found in the littoral sands of Australia, where the zones richest in titanium extend over 500-600 km of the continent's eastern shoreline.

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The belt of beach and dune sands of Australia is comparatively narrow, but reaches a width of about 800 m in spots. The sands consist of quartz (which composes their basic mass), zircon, rutile, leucoxenized ilmenite, leucoxene, and insignificant quantities of monazite [(Ce, La)PO<sub>4</sub>], garnet, magnetite, chromite, and cassiterite.

The average content of heavy minerals in the beach sands is 5-6%. The heavy slime contains an average of 30.2% rutile, 38.8% zircon, 26.5% ilmenite, 0.5% monazite, and 4% other minerals. Most of the ore grains have sizes ranging from 0.1 to 0.14 mm. In 1963, about 172 thousand tons of rutile concentrates and 184 thousand tons of ilmenite concentrates were extracted from these sands.

In addition to the beach sands, Australia has rich deposits of dune and underground placers. They are not as rich in titanium (their average heavy-mineral content is ~3%), but they are thicker. Alluvial titanium deposits include many deposits in India, Indonesia, South America, the USA, and elsewhere.

A unique alluvial deposit in the USSR is the Samotkan' deposit of zircon-rutile-ilmenite ores in the central Dnepr region. The Samotkan' deposit is a buried marine placer that was apparently formed by a littoral submarine current. This deposit is uncommonly thick as compared with the beach deposits of Australia and other countries. The degree of leucoxenization in the ilmenite of this deposit is extremely high. A. V. Rudneva [10, page 10] reported that 80% of the concentrate obtained from the Samotkan' placers has a mineralogical composition similar to that of arizonite. The littoral-submarine formations of the poltavna and Sarmatian stages appeared during the shaping of a thick Mesozoic chemical-alteration crust. Crystalline rocks underlying the deposit occur at depths of more than 100 m. The poltavna suite is a monotonous stratum of fine-grained light gray and yellowish-gray quartz sands ranging up to 30-40 m in thickness (the sheets vary from 5 to 40 m in thickness). This zone is overlaid by clayey sands and greenish-gray Sarmatian clays 20-25 m deep.

The poltavan and Sarmatian sands contain zirconium, rutile, and ilmenite.

In the poltavan sands, the heavy-mineral yield with densities above 2.9 varies from 0.5 to 300 kg/m<sup>3</sup>. Higher heavy-mineral contents are found in the upper-level fine-grained sands. The middle and lower poltavan sands are distinguished by lower heavy-mineral contents, but they have occasional lenses of commercially valuable sands.

The ore-grain sizes vary from 0.05 to 0.12 mm; the ilmenite grains are larger than those of rutile and zirconium. The size of the quartz grains is about 0.2 mm.

The electromagnetic fraction of the sands makes up 50-60% of the heavy fraction and consists of 65-70% strongly leucoxenized ilmenite (resembling arizonite), 20-35% staurolite, 1-5% tourmaline, and such admixtures as spinels, manganandalusite, and others. The nonelectromagnetic fraction contains 20-40% rutile, 15-45% zircon, and 5-10% leucoxene, 10-40% sillimanite, and 5-10% disthene, with anatase, andalusite, and corundum admixtures.

The deeper layers of the Sarmatian fine-grained sands are enriched in ore materials. Heavy slime from the Sarmatian sands contains about 13-17% rutile, 32-37% ilmenite, 9-11% zircon, and about 40% nonmetallic minerals - disthene, sillimanite, staurolite, and tourmaline. The minerals are well nodulized and coarser than those found in the poltavan sands.

The Tobolsk deposit of zircon-rutile-ilmenite ores in the Transural region, which was discovered in 1954, is a beach placer, again of marine origin, and contains about 80% ilmenite, 10% rutile, and 9% zircon.

The large Irsha alluviofluvial ilmenite deposit occurs in the Volyn' gabbroanorthosite region; its ilmenite content is somewhat more than 20 kg/m<sup>3</sup> of excavated mass, with a heavy-concentrate yield of 1.4 to 711 kg/m<sup>3</sup>. The titanium dioxide content varies from 49 to 60% in the leucoxenized ilmenite, averaging 50-52%.

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All of the titanium-ore deposits listed above are of the composite rutile-ilmenite-zircon ore iron-titanium-vanadium types. Concentration of these ores yields an iron-titanium concentrate, which is then further enriched metallurgically, by smelting in ore furnaces to rich titanium slag and pig iron. If a rutile concentrate is used for extraction of titanium, the smelting-furnace process is unnecessary. Rutile ores occur in the so-called metamorphogenous deposits. Although these deposits have not been studied very thoroughly, they will obviously become an important source of supply of rutile concentrate for the titanium industry.

#### Concentration of Titanium Ores

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The following scheme is usually used in concentration of alluvial ores: washing and size classification of the sands, extraction of a combined rutile-zircon concentrate on screw separators or concentration tables, improvement of the crude concentrate by electrostatic separation into ilmenite, rutile, and zircon concentrates. Flotation is sometimes used to extract the zircon concentrate.

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Process flow charts for concentration of ores from native titanium-magnetite deposits usually include staged crushing with screening, closed-cycle grinding with classification, and gravitational concentration with improvement of the crude concentrate by magnetic separation.

#### Concentration of Australian Sands

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Exploitation of Australian deposits began in 1931-1932. In 1934, work was begun at the first concentration plant at Byrro Bay, which used flotation to extract the zircon. All subsequently built plants use concentration on tables and electrostatic methods of rutile extraction instead of flotation.

At the present time, the Byron Bay plant produces high-quality rutile, ilmenite, and zircon concentrates, as well as such byproducts as monazite concentrate, washed silicate sand, classified garnet, and a small amount of tin concentrate. Most

of the concentrates extracted in Australia are exported to the USA and Japan.

Primary processing of the sands is on tables or screw separators. Wilfley tables are usually used. The density distribution of the sands is quite clear-cut; the upper fraction is a narrow strip of monazite head with cassiterite, followed by zones of zircon, ilmenite, and rutile and then by minerals with densities of 3-4 g/cm<sup>3</sup> and a bottom fraction of quartz with a rutile admixture, which must be subjected to secondary cleaning. Up to 5% of rutile is present in the 3-4-g/cm<sup>3</sup> fraction.

The monazite head contains small quantities of garnet, spinels, or tourmaline. A monazite concentrate containing 92-98% monazite can be obtained by electromagnetic separation and subsequent cleaning up on tables.

The intermediate-density fraction is sent to the tailings and returned to the seacoast for natural classification.

The Stradbroke Island plant, like a number of others, uses Tampfrey screw separators, which give a higher heavy-mineral extraction, for the primary processing of the sands. Fifty Tampfrey separators, each with a capacity of 0.8-1 ton/hour, are used for the basic concentration stage. In this stage, processing of sands containing about 6% heavy minerals produces a concentrate containing more than 24% heavy minerals. This product is further refined on 12 similar units to produce a concentrate containing up to 90% of heavy minerals. This concentrate is then rerefined with selective concentration.

Before separation of the zircon, rutile, and ilmenite, the resulting collective concentrate is dried in rotary driers. After cooling to about 80°C, the concentrate is sent for separation. Usually, combination concentration processes are used to separate the collective concentrate, including magnetic and electrostatic separation. Ilmenite has the highest susceptibility in the collective concentrate, and monazite is second in this respect. Zircon and rutile are nonmagnetic. In occasional cases, however, a variety of rutile with weak magnetic properties is observed. In

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the presence of films of ferrous compounds, zircon also shows weak magnetic properties.

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Almost all plants on the east coast of Australia are equipped with induction-type roller separators with high magnetic fields. The Escolon separator, which is usually made duplex with two or three poles on each side, is most commonly used. This separator can operate with high and low magnetic field strengths and with a 6.5-A load at 120 V.

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Electrostatic separation is based on the differences between the electrical conductivities of the minerals. They can be arranged in the following series in order of diminishing conductivity: magnetite, ilmenite, rutile, chromite, leucoxene, garnet, monazite, tourmaline, zircon, and quartz.

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Septon Steel and Steel Machines roller separators are usually used for electrostatic separation; there are also considerable numbers of separators of various types that have been built on site.

Electrostatic-separator rollers are made from bronze or steel pipes from 125 to 172 mm in diameter and 915 to 2440 mm in length. The rollers turn at 300 to 600 rev/min. The potential difference between the electrode and the roller is varied from 16 to 40 thousand volts.

Separators with 28 rollers cascaded in two rows are used at the Associated Minerals concentration plant. Rutile concentrate is extracted on the upper seven rollers, and an intermediate product on the lower seven (in addition, a zircon concentrate is obtained on the three lower rollers). Such separators produce 360-720 kg per hour per meter of roller length.

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Magnetic and electrostatic separations take different positions in process flow at different plants. Recently, electrostatic separation has usually been at the head of the chart. The installation of Mineral Deposits Syndicate may serve as an example for this placement of the separators.

At the Zircon Rutile Limited plant, zircon is separated from the collective concentrate by flotation, with addition of eucalyptus oil as a frothing agent. This process extracts 95-97% of the zircon. This particular plant produces a rutile concentrate containing 97.75% of titanium dioxide. As we noted above, flotation is no longer used at the newer plants.

Concentration of Titanomagnetites from the Kusa Deposit

The enrichment flow chart used at the Kusa concentration plant is characteristic for concentration of native rocks. As we noted earlier, the titanomagnetites of this deposit present a polymetallic ore consisting basically of vanadium-bearing magnetite and ilmenite.

TABLE 14  
Concentration Data for Titanomagnetite Ores of Kusa Deposit

| concentrate                        | distrib-<br>ution<br>% | content, %   |                  |                               |           | extraction, % |                  |                               |
|------------------------------------|------------------------|--------------|------------------|-------------------------------|-----------|---------------|------------------|-------------------------------|
|                                    |                        | Fe           | TiO <sub>2</sub> | V <sub>2</sub> O <sub>5</sub> | Co        | Fe            | TiO <sub>2</sub> | V <sub>2</sub> O <sub>5</sub> |
| iron-vanadium<br>ilmenite, . . .   | 54.0<br>19.5           | 64.0<br>36.0 | 5.5<br>45.0      | 0.90<br>0.25                  | —<br>—    | 74.3<br>15.0  | 22.8<br>67.4     | 83.8<br>8.4                   |
| pyrite (cobalt)<br>tailings, . . . | 0.2<br>26.3            | 36.0<br>18.5 | 3.4<br>4.5       | 0.25<br>0.17                  | 0.58<br>— | 0.2<br>10.5   | 0.06<br>9.76     | 0.1<br>7.7                    |

The Kusa ore has the following mineralogical composition: 60-70% magnetite, 20-30% ilmenite, 2-10% chlorite, and small quantities of iron glance and pyrites [10, pages 10, 11].

In the first concentration stage, the ore is subjected to wet magnetic separation in drum-type separators after crushing to 25 mm and smaller. Ore containing 41.3% of iron and 10% titanium dioxide produces a concentrate containing 46.6% iron and 12.6% titanium dioxide. The collective concentrate is fine-ground to 1.5-2% mesh +40, with subsequent wet magnetic separation on SE128B belt separators. The intermediate products are returned for re-processing.

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The wet magnetic separation produces an iron-vanadium concentrate and a titanium intermediate product, which is subjected to flotation after separation of sludge and condensation in hydraulic cyclones. Pyrite flotation with addition of 200 g/ton of sulfuric acid, 200 g/ton of xanthogenate, and 40 g/ton of flotation oil is provided for acquisition of a low-sulfur ilmenite concentration. Soda is introduced into the pulp to soften the water. Up to 95% of titanium dioxide is extracted in the concentrate.

Data on concentration of the Kusa titanomagnetites according to [12, 13] are given in Table 14.

Prototype Concentration Flow Chart for Titanium-Zirconium Sands of Marine Origin

A prototype flow chart has been developed for the concentration of titanium-zirconium sands of marine origin [14]. Here the basic mineralogical fractions are represented basically by ilmenite, rutile, leucosene, zircon, disthene, sillimanite, and stauroilite. Companion minerals are tourmaline, chromite, spinels, garnets, corundum, andalusite, chlorite, and monazite. The light fractions are quartz and clays. The granulometric composition of the sands is characterized by the following data:

| Fraction, mm | Yield of fraction, % |
|--------------|----------------------|
| +0.5         | 0.4                  |
| -0.5+0.25    | 8.2                  |
| -0.25+0.15   | 34.8                 |
| -0.15+0.10   | 35.7                 |
| -0.10+0.07   | 2.0                  |
| -0.07        | 18.9                 |

The mass per unit volume of the sands in the bed is 1.9-2.15 tons/m<sup>3</sup> at a moisture content of 5.6-12.3%. The ilmenite grain sizes vary from 0.25 to 0.07 mm, those of rutile from 0.25 to 0.06, and those of zircon from 0.15 to 0.06 mm. Grain sizes are inversely proportional to the densities of the minerals.

Figure 5 shows the process flow chart for a concentration plant.

The preparatory operations include disintegration and desliming. Disintegration is carried out in 1600 x 7630-mm vat

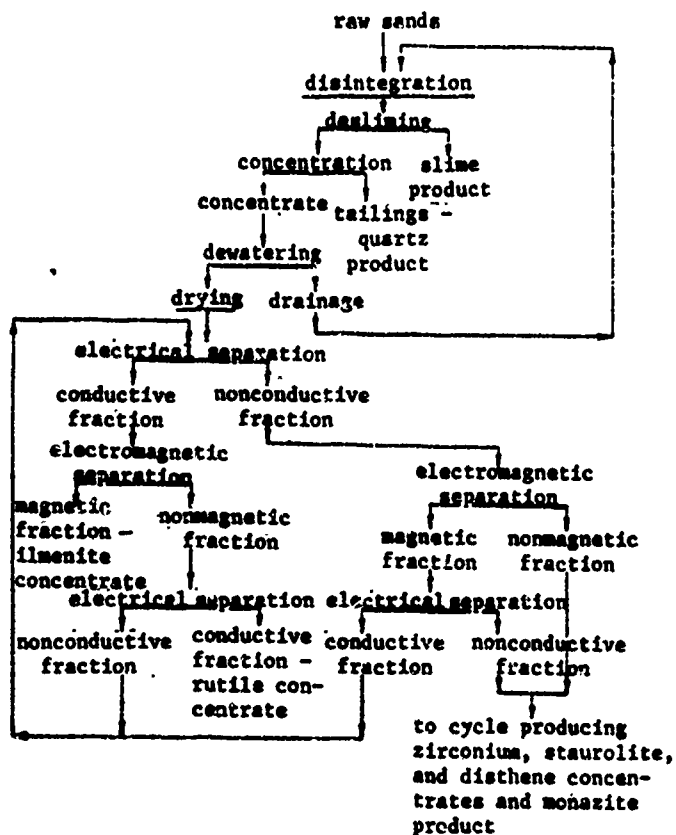


Figure 5. Concentration flow chart for titanium-zirconium sands [14].

washers. The desliming process uses 3000 x 8500-mm rake classifiers with hydraulic control cyclones at the discharge. Rake classifiers are used to wring out the washed product and spread the sand out over the tables. The primary concentration takes place on 211 type YaSK-1 three-level concentration tables. Of these, 136 are used for primary concentration, 40 to concentrate

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the intermediate products, and 18 to rerefine the concentrate. The resulting collective concentrate is finished by electric separation, magnetic separation, and gravity concentration on tables for the zircon.

The collective concentrate is wrung out in one- and two-spiral classifiers with a vacuum-drainage system. This reduces concentrate moisture content to 8%. The two-spiral classifiers have the dimensions 1200 x 8400 mm, while the single-spiral machines are 1000 x 6500 mm.

The concentrates are dried in two 2200 x 16,000 mm drum-type driers and three 1600 x 8000-mm natural-gas-fired driers.

Electrical separation is effected on 113 EKS-1250 separators, of which 82 are used for crude concentrate, 13 for control separation of the rutile concentrate, 10 for control of the staurolite product, and 8 for control of the zirconium concentrate.

Twelve NIGRI-2VK-5 induction-roller separators are used for magnetic separation. Of these, 7 separators are used for primary separation and 5 for refining.

The nonconductive fraction is subjected to reworking on 28 MS-2 pan-disk electrostatic separators. The nonmagnetic fraction from these separators is pumped to the gravity cycle through 1000 x 6500-mm buffering spiral classifiers and dust separators. The plant flow chart also provides for the preparation of disthene-sillimanite, staurolite, and monazite concentrates.

#### Titanium Concentrates

Concentrates with high titanium oxide contents can be produced by concentration. Four concentrate grades are used in the Soviet Union: rutile, ilmenite, rutilized, and arizonite [4, page 8; 10, page 105; 15; 18]. Table 15 lists the compositions of these concentrates.

The rutile and arizonite concentrates are richest in titanium dioxide. Rutile concentrate is produced in comparatively small quantities in the USSR.

TABLE 15  
Chemical Compositions of Soviet Titanium Concentrates, %

| component  | arizonite                 |                            | rutil-<br>ized<br>ilmenite | ilmenite          | rutile                          |
|--|---------------------------|----------------------------|----------------------------|-------------------|---------------------------------|
|  | first<br>compo-<br>sition | second<br>compo-<br>sition |                            |                   |                                 |
| TiO <sub>2</sub>   | 60,3<br>65,31<br>63,0     | 69,0<br>65,3<br>61,3       | 50,78<br>—<br>—            | 42,0<br>—<br>—    | 93,2<br>—<br>—                  |
| Fe <sub>2</sub> O <sub>3</sub>                                   | 25,88<br>27,88<br>26,4    | 23,1<br>28,4<br>26,6       | 12,0<br>—<br>—             | 13,8<br>—<br>—    | 1,8 Fe <sub>tot</sub><br>—<br>— |
| FeO  | —                         | —                          | 33,2                       | 32,9              | —                               |
| Al <sub>2</sub> O <sub>3</sub>                                   | 2,0<br>3,50<br>2,45       | 2,18<br>3,0<br>2,50        | 1,47<br>—<br>—             | 2,75<br>—<br>—    | 1,1<br>—<br>—                   |
| Cr <sub>2</sub> O <sub>3</sub>                                   | 1,36<br>4,48<br>2,55      | 2,80<br>5,18<br>3,93       | —<br>—<br>—                | —<br>—<br>—       | 0,27<br>—<br>—                  |
| SiO <sub>2</sub>   | 1,20<br>4,20<br>2,14      | 1,10<br>2,40<br>1,79       | 1,33<br>—<br>—             | 3,50<br>2,44<br>— | 2,0<br>—<br>—                   |
| CaO  | 0,17<br>0,60<br>0,34      | 0,20<br>2,40<br>0,30       | traces<br>—<br>—           | 0,77<br>1,35<br>— | 0,22<br>—<br>—                  |
| MgO  | 0,2<br>2,0<br>1,32        | 0,99<br>1,50<br>1,23       | 0,60<br>—<br>—             | 2,80<br>—<br>—    | —<br>—<br>—                     |
| MnO  | 0,85<br>1,15<br>0,98      | 0,90<br>1,07<br>0,99       | 0,54<br>—<br>—             | 0,77<br>—<br>—    | 0,18<br>—<br>—                  |
| V <sub>2</sub> O <sub>5</sub>                                    | traces<br>0,12<br>0,08    | traces<br>0,08<br>0,07     | 0,88<br>—<br>—             | 0,25<br>—<br>—    | 0,13<br>—<br>—                  |
| ZrO <sub>2</sub>   | —                         | —                          | —                          | —                 | 2,5                             |
| S  | 0,1-0,18                  | —                          | 0,03-0,05                  | 0,4               | —                               |
| other oxides   | 0,74                      | 0,75                       | —                          | 0,46              | —                               |
| sum of TiO <sub>2</sub> ,<br>FeO, Fe <sub>2</sub> O <sub>3</sub> | 82,4                      | 84,4                       | 95,88                      | 88,79             | —                               |

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The arizonite concentrate is characterized by high chromium- and manganese-oxide contents. As a rule, the monomineral arizonite contains the following impurities, which are included into its lattice: from 0.05 to 1.75%  $\text{Cr}_2\text{O}_3$ , up to 0.4%  $\text{V}_2\text{O}_5$ , from 0.08 to 0.17%  $\text{MnO}$ , and 0.8-0.9%  $\text{MgO}$ .

The rutilized concentrate is quite rich in  $\text{TiO}_2$ ; it also contains minimal amounts of the most undesirable admixtures. In the USSR, this concentrate is extracted from alluviofluvial placer deposits. Owing to the low chromium contents, it is of particular value for the titanium-pigment industry.

TABLE 16

Minerological Compositions of Titanium Concentrates, %

| mineral             | formula   | arizonite | rutilized ilmenite | ilmenite | rutile |
|---------------------|---|-----------|--------------------|----------|--------|
| ilmenite . . .      | $\text{FeTiO}_3$  | —         | —                  | 75-80    | —      |
| arizonite . . .     | $\text{Fe}_2\text{O}_3 \cdot 3\text{TiO}_2$   | 80-90     | —                  | —        | —      |
| rutile . . . . .    | $\text{TiO}_2$  | —         | 25.4-27            | —        | 86.5   |
| zircon . . . . .    | $\text{ZrO}_2 \cdot \text{SiO}_2$   | 0.3       | —                  | —        | 0.3    |
| crichtonite . . .   | $\text{FeTiO}_3$  | —         | 51.20              | —        | —      |
| leucosene . . . .   | $\text{TiO}_2$  | 3.13      | —                  | —        | 12.9   |
| magnetite . . . .   | $\text{Fe}_3\text{O}_4$   | —         | —                  | 1-2      | —      |
| hematite . . . .    | $\text{Fe}_2\text{O}_3$   | 0-5.5     | 17.710             | —        | —      |
| chlorite . . . . .  | $(\text{Mg}, \text{Fe})_{2-3}(\text{Al}, \text{Fe})_{2-3}(\text{OH})_2 \cdot \text{Al}_2\text{Si}_{2-3}\text{O}_{10} \cdot \text{H}_2\text{O}$<br>$x = 0.3-1$ | —         | —                  | —        | —      |
| biotite . . . . .   | a magnesium-iron mica   | —         | —                  | 1-2      | —      |
| garnet . . . . .    | $\text{R}_2^{2+} \text{R}_2^{3+} (\text{SiO}_3)_3$  | —         | —                  | 5        | —      |
| staurolite . . . .  | $(\text{Ca}, \text{Mn})\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot x$<br>$x = 2\text{SiO}_2 \cdot \text{H}_2\text{O}$   | 3.2-4.7   | —                  | —        | —      |
| disthene . . . . .  | $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  | —         | —                  | —        | 0.3    |
| chroma spinellide   | $(\text{Mg}, \text{Mn})\text{O}(\text{Al}, \text{Cr})_2\text{O}_3$  | 2-5.5     | —                  | —        | —      |
| quartz . . . . .    | $\text{SiO}_2$  | —         | —                  | 1.0      | —      |
| geikiehlite . . . . | $\text{MgO} \cdot \text{TiO}_2$   | —         | 2.21               | —        | —      |
| pyrophanite . . . . | $\text{MnO} \cdot \text{TiO}_2$   | —         | 1.280              | —        | —      |
| silicates . . . . . | —   | —         | 2.14               | —        | —      |
| sulfides . . . . .  | —   | —         | 0.05               | —        | —      |

Table 16 gives the minerological compositions of various titanium concentrates [4, page 10; 105; 15; 16]. As the data indicate, all four concentrate types differ in minerological

TABLE 17

Typical Chemical Compositions of Certain Foreign Ilmenite Concentrates and Slags  
[18], %

| Component                      | Australia            |                      |        | Canada |                  | India   |        |         | USA    |           |                      |         |                |               |
|--------------------------------|----------------------|----------------------|--------|--------|------------------|---------|--------|---------|--------|-----------|----------------------|---------|----------------|---------------|
|                                | 1st com-<br>position | 2nd com-<br>position | Brazil | Slag   | Concen-<br>trate | Chavara | Monako | Lakshet | Quilon | Amam      | SCARANGET,<br>NORWAY | Florida | Plney<br>River | Teja-<br>Vios |
| Y <sub>2</sub> O <sub>3</sub>  | 44-53                | 28,12                | 48,2   | 70,8   | 41,98            | 60,03   | 54,0   | 54,0    | 60,4   | 51-55     | 44,40                | 57,80   | 44,0           | 44,5          |
| Fe <sub>2</sub> O <sub>3</sub> | 10-13                | 14,15                | 16,6   | —      | 16,04            | 24,77   | 17,0   | 17,0    | 24,9   | 8-18      | 13,44                | 24,60   | 13,30          | 5,3           |
| P <sub>2</sub> O <sub>5</sub>  | 31-33                | 20,04                | 22,4   | 6,8    | 20,30            | 9,67    | 20,0   | 2,7     | 2,7    | 20-23     | 26,00                | 12,30   | 26,20          | 20,1          |
| Al <sub>2</sub> O <sub>3</sub> | —                    | —                    | 0,3    | 6,3    | 2,70             | —       | —      | 1,30    | —      | —         | —                    | 1,24    | —              | 3,0           |
| MgO                            | —                    | 1,61                 | 0,6    | 0,24   | 0,10             | 0,47    | 0,40   | 0,44    | 0,44   | 2,5-4,5   | —                    | —       | —              | 0,3           |
| CaO                            | —                    | —                    | 0,1    | 1,1    | 0,40             | —       | —      | 0,08    | —      | —         | —                    | 0,04    | —              | 1,0           |
| Na <sub>2</sub> O              | —                    | —                    | —      | —      | 0,01             | —       | —      | —       | —      | —         | —                    | —       | —              | —             |
| K <sub>2</sub> O               | —                    | —                    | —      | —      | —                | —       | —      | —       | —      | —         | —                    | —       | —              | —             |
| ZnO                            | —                    | 0,28                 | 0,1    | —      | 6,30             | —       | —      | —       | 0,73   | —         | 3,55                 | —       | —              | —             |
| Cr <sub>2</sub> O <sub>3</sub> | 5-5,5                | 0,04                 | 0,5    | 0,20   | 0,20             | 0,18    | 0,05   | 0,05    | 0,05   | 0,03-0,10 | 0,01                 | —       | 0,03           | 2,0           |
| V <sub>2</sub> O <sub>5</sub>  | —                    | 0,16                 | 0,06   | 0,46   | 0,18             | 0,20    | 0,18   | 0,08    | 0,08   | 0,03-0,10 | 0,18                 | —       | 0,09           | 0,15          |
| Zn                             | —                    | —                    | 0,1    | —      | 0,76             | 0,76    | 0,83   | —       | —      | —         | —                    | —       | 0,22           | 0,10          |
| S                              | —                    | —                    | —      | 0,20   | —                | —       | —      | —       | —      | —         | —                    | 0,01    | —              | —             |
| P <sub>2</sub> O <sub>5</sub>  | —                    | —                    | —      | —      | —                | 0,15    | 0,23   | 0,23    | 0,2    | 0,1-0,3   | 0,02                 | 0,03    | 0,02           | 0,01          |
| SiO <sub>2</sub>               | —                    | 0,16                 | 1,4    | 0,1    | 2,56             | 0,71    | 1,15   | 1,15    | 0,76   | 2,0       | 2,70                 | 3,14    | 1,40           | 3,0           |
| H <sub>2</sub> O               | —                    | —                    | —      | —      | —                | 1,20    | 2,0    | 2,0     | —      | —         | —                    | —       | —              | —             |

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TABLE 18

Typical Chemical Compositions of Rutile Concentrates Produced Abroad, %

| component                      | Florida | Travan-<br>core<br>(India) | Came-<br>rooms | Australia            |                      |
|--------------------------------|---------|----------------------------|----------------|----------------------|----------------------|
|                                |         |                            |                | 1st com-<br>position | 2nd com-<br>position |
| TiO <sub>2</sub>               | 93.64   | 98.42                      | 97.51          | 95.74                | 96.77                |
| Fe <sub>2</sub> O <sub>3</sub> | 2.56    | 1.14                       | 0.64           | 0.60                 | —                    |
| FeO                            | —       | —                          | —              | —                    | 0.55                 |
| Al <sub>2</sub> O <sub>3</sub> | 0.46    | —                          | —              | 1.25                 | 0.14                 |
| MnO <sub>2</sub>               | 0.05    | —                          | 0.08           | —                    | —                    |
| CaO                            | 0.02    | —                          | 0.15           | 0.04                 | —                    |
| Na <sub>2</sub> O              | 0.01    | 0.60                       | 0.30           | 0.30                 | —                    |
| MgO                            | 0.05    | —                          | 0.29           | 0.04                 | —                    |
| Cr <sub>2</sub> O <sub>3</sub> | 0.14    | 0.30                       | 0.10           | 0.06                 | 0.16                 |
| V <sub>2</sub> O <sub>5</sub>  | 0.29    | —                          | —              | —                    | —                    |
| S                              | —       | 0.20                       | —              | 0.05                 | —                    |
| P <sub>2</sub> O <sub>5</sub>  | 0.10    | 0.04                       | 0.98           | 0.12                 | —                    |
| SiO <sub>2</sub>               | 1.02    | 0.43                       | 0.25           | 0.60                 | 2.23                 |
| ZrO <sub>2</sub>               | 1.46    | —                          | —              | —                    | —                    |
| H <sub>2</sub> O               | 0.12    | 0.29                       | 0.24           | 0.17                 | —                    |

composition. This causes them to behave differently when the iron oxides are reduced in subsequent metallurgical processing.

We list below certain physical properties of the titanium concentrates [10, page 105; 15; 18].

|  | Arizonite | Rutilized | Ilmenite  |
|--|-----------|-----------|-----------|
| Density, g/cm <sup>3</sup>                                   | 3.96      | 4.27-4.28 | 4.22      |
| Bulk mass, tons/m <sup>3</sup>                               | 2.10-2.11 | 2.94-2.96 | 2.34-2.35 |
| Bulk mass after shake-down, tons/m <sup>3</sup>              | 2.19-2.21 | 3.13-3.17 | —         |
| Initial sintering temperature, °C                            | 1350      | 950-1000  | 850-900   |
| Concentrate resistivity, Ω/cm <sup>3</sup> × 10 <sup>5</sup> | >4        | 5.75      | 1.38      |
| Granulometric composition, % at grain sizes of, in mm:       |           |           |           |
| +0.5 . . . . .   | 0.05      | 25.93     | 0.25      |
| -0.5+0.2 . . . . .   | 0.50      | 41.11     | 28.44     |
| -0.2+0.15 . . . . .  | 5.70      | 17.16     | 19.07     |
| -0.15+0.12 . . . . .   | 49.05     | 3.25      | 29.09     |
| -0.12 . . . . .  | 49.05     | 2.84      | 29.74     |

Table 17 gives the compositions of certain ilmenite concentrates produced abroad, and Table 18 those of foreign rutile concentrates [19].

The mineralogical compositions of the domestic concentrates (see Table 16) indicates that they contain individualized minerals that do not contain titanium. They include staurolite and chrome spinel in the arizonite concentrate; geikielite, pyrophanite, and silicates in the rutilized concentrate; chlorite, biotite, garnet, and quartz in the ilmenite concentrate. Research has shown that these nonmetallic minerals can be removed from the concentrates by secondary purification. One of the possible methods is reductive magnetizing annealing of the concentrate with subsequent magnetic separation. This removes about 50% of the nonmetallic minerals in the nonmagnetic fraction, the yield of which is 5-10% [4, page 8].

Further repurification of the concentrates increases their cost, but the investment is returned in the chlorination process by the higher extraction of titanium, higher equipment productivity, and improved quality of the titanium tetrachloride.

A method has also been proposed for acquisition of technical titanium dioxide from arizonite concentrate with a composition approaching that of the rutile concentrate.<sup>(1)</sup> In this method, the crushed arizonite concentrate is subjected to reductive annealing with natural gas (in a fluidized bed at 800-1000°C). Since undiluted natural gas is used in this process, 92-96% of the iron oxides are reduced to the metal. The reduced concentrate is then leached in dilute acid, and the product, which contains 90-95% of titanium dioxide, is used to produce titanium tetrachloride.

This process is economically justifiable for concentrates containing relatively small amounts of iron.

As a result, a product similar to rutile concentrate is obtained from the ilmenite or arizonite concentrate.

Titanium concentrates can be further enriched by ordinary electrostatic separation. Then, however, 10-20% of titanium dioxide goes into the intermediate product, and this makes its subsequent refinement more difficult.

All of these new methods are under development. Only the process in which the concentrates are smelted to produce rich titanium slags and pig iron has come into extensive use in industry. Footnote (1) appears on page 84.

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<sup>1</sup>Author's certificate (USSR) No. 174,363, 1965.

Chapter 7

PHYSICO-CHEMICAL FUNDAMENTALS OF THE ELECTROTHERMAL  
REDUCTION OF TITANIUM CONCENTRATES

Metallic titanium is now produced chiefly from titanium tetrachloride. There is also a trend toward the production of pigment titanium dioxide from titanium tetrachloride. For this reason, the industrial ore raw material must have a composition that meets the requirements of the chlorination process.

The smaller the amount of impurities entering the chlorinator, the higher will be the extraction of titanium in the purified titanium tetrachloride; chlorine consumption will also be lower, working conditions will be improved, and the net cost of the titanium tetrachloride will be reduced. Direct chlorination of ilmenite concentrate so complicates the process of chlorination and purifying the resulting  $TiCl_4$  from the large amount of impurities that it is more advantageous in practice to separate the iron from the concentrate before chlorination. This is now done by smelting the ilmenite to rich titanium slag, with reduction of the iron oxides to the metal [10, page 82; 11; 19]. Pig iron and titanium slags are the commercial products from ilmenite-concentrate smelting. The net cost of the slag is reduced substantially when useful pig iron is produced.

Metallurgists were long ago attracted by the possibility of concentrating titanium oxides by metallurgical methods. Early

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studies of titanomagnetite smelting in blast furnaces demonstrated the practical feasibility of producing a titanium-rich fluid slag [19-21]. The first Russian studies of electric smelting of ilmenite concentrates were carried out in 1917 by M.S. Maksimenko [15]. Titanium slags were produced by ore-reduction smelting of an ilmenite concentrate containing 49.17%  $TiO_2$ .

In 1929, S.S. Shteynberg and P.S. Kusakin experimented with smelting of titanium ore in an electric furnace to produce ferrotitanium [22]. Ilmenite with a content of 52.3%  $TiO_2$  and titanomagnetite containing 14.1%  $TiO_2$  were used for the melts. The resulting slag contained 78-82%  $TiO_2$ , with iron and manganese oxides making up the remainder.

M.N. Sobolev described certain other experiments in the electric smelting of titanium magnetites [23]. Industrial studies made at the Zaporosh'ye Ferroalloys Plant laid the foundations for systematic research toward a process for acquisition of rich titanium slags [16; 19; 24, pages 16 and 23].

#### Reduction of Iron Oxides from Titanium-Bearing Minerals

It was assumed early in the research that ilmenite dissociates into  $FeO$  and  $TiO_2$  during the reduction process. However, subsequent x-ray structural analyses indicated that this dissociation does not occur.

G.I. Chufarov and Ye.P. Tatiyevskaya [25] investigated the reduction kinetics of ilmenite for gaseous and solid reducing agents. Reduction of pure titanium dioxide was also studied for comparison. The experiments were conducted in a vacuum with continuous pumping of the gaseous reaction products by high-vacuum pumps. It was established that the reduction of ilmenite begins at considerably higher temperatures than the reduction of ferrous oxide.

It was also found that the reduction of ilmenite and titanium dioxide by graphite proceeds slowly. Only 85% of the ferrous oxide had been reduced to the metal in ilmenite held for 15 hours at 1150°C. Under the same conditions, only 4.5% of titanium dioxide had been reduced after 18 hours.

It was established that in the presence of gaseous reaction products (mainly CO), the reduction rate increases to some degree for ilmenite and titanium dioxide. Increasing the carbon monoxide partial pressure also accelerates reduction. Reduction by carbon monoxide proceeds more rapidly in the presence of graphite than in its absence. The authors explain this in terms of the reaction of carbon dioxide with carbon, which increases the CO partial pressure, thus helping accelerate the reduction process.

Reduction rate is shown as a function of the nature of the reducing agent in Fig. 6 for ilmenite and Fig. 7 for titanium dioxide.

We see from these figures that the titanium dioxide present in ilmenite is reduced to  $Ti_2O_3 \cdot TiO_2$  considerably more easily than pure titanium dioxide.

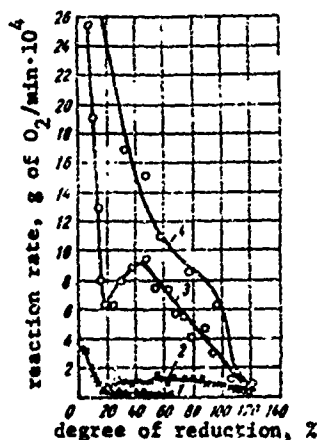


Figure 6. Rates of reduction of ilmenite by various reducing agents at 1100°C. 1) Graphite in vacuum; 2) graphite with accumulation of gaseous products in reactor; 3) carbon monoxide at pressure of 150 mm Hg; 4) graphite with carbon monoxide at pressure 150 mm Hg.

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With a large graphite excess and rubbing out after each experiment, titanium dioxide could be reduced to  $Ti_2O_3 \cdot TiO_2$  only at 1150°C.

On the basis of their data, the authors concluded that ilmenite is reduced by carbon monoxide, and that this process advances without decomposition of the ilmenite into its components. Here the reduction of the ferrous oxide accelerates the reduction of the titanium dioxide associated with it.

In the case of vacuum reduction of manganese oxides and ilmenite, the authors demonstrated an inhibiting effect of  $SiO_2$ ,  $Al_2O_3$ , and  $Fe_3O_4$  additives that results from the smaller reaction surface presented by the chemical

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reaction rate, g of O<sub>2</sub>/min · 10<sup>4</sup>

Figure 6. Rates of reduction of ilmenite by various reducing agents at 1100°C. 1) Graphite in vacuum; 2) graphite with accumulation of gaseous products in reactor; 3) carbon monoxide at pressure of 150 mm Hg; 4) graphite with carbon monoxide at pressure 150 mm Hg.

studied were varied to 1700°C. Reaction products include iron, titanium, and manganese oxides and carbonates. Footnote: FTD-HC-

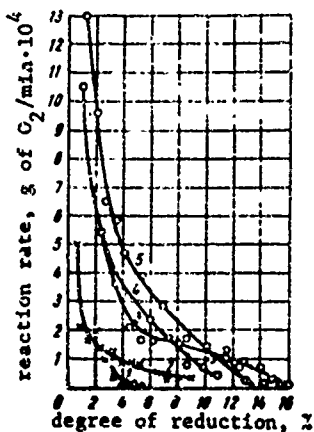


Figure 7. Rates of reduction of titanium dioxide by various reducing agents 1) Graphite in vacuum at 1150°C; 2) carbon monoxide at 1100°C and pressure of 150 mm Hg; 3) graphite at 1150°C, with accumulation of gaseous products in reactor (weighed specimen with  $TiO_2:C$  ratio of 1:1.5); 4) graphite and carbon monoxide at 1150°C and pressure of 150 mm Hg; 5) hydrogen at 1100°C and pressure of 150 mm Hg.

studied as the proportions of ilmenite and titanium sesquioxide were varied from 0.1:1 to 4:1 and temperature was varied from 1300 to 1700°C. It was established that up to a ratio of 0.5:1, the reaction takes place in the solid solution with formation of metallic iron. This reaction is preceded by formation of the mineral tagirovite ( $FeO \cdot TiO_2 \cdot Ti_2O_3$ ). Beginning at proportions of 0.5:1 and extending to 1.5:1, reduction is accompanied by formation of anosevite [ $(Fe, Mg, Mn)O \cdot 2TiO_2 \cdot Ti_3O_5$ ].<sup>(1)</sup> Here, there are no tagirovite or ilmenite phases. Beginning at proportions of 2:1 and up

Footnote (1) appears on page 109.

compounds that form - silicates, aluminates, and ferrites. On the other hand, alkali-metal salts, and potash in particular, have a strong activating effect on the reduction of ilmenite.

These hypotheses were confirmed by work done at the A.A. Baykov Institute of Metallurgy. It was shown that the reduction of ferrous oxide from ilmenite is accompanied by reduction of titanium dioxide to lower oxides [19]. The free energies of the reactions that take place here and those of the reactions in which titanium oxides are formed from the elements are given in Table 19.

A.V. Rudneva established that the titanium sesquioxide formed in the reduction process dissolves in the ilmenite lattice [26, 27]. The reaction of natural ilmenite, which corresponds to the formula  $3FeO \cdot TiO_2 \cdot Fe_2O_3$ , with titanium sesquioxide was investigated in [28, page 75]. The change in phase composition was

TABLE 19  
Variation of Free Energies for Certain Reactions

| reaction  | $\Delta F$ cal/<br>(deg. g. mole)  | liter-<br>ature<br>source |
|---|--|---------------------------|
| $FeO \cdot TiO_2 + C = Fe + TiO_2 + CO$<br>$\frac{1}{2} FeO \cdot TiO_2 + C = \frac{1}{2} Fe + \frac{1}{2} Ti_2O_3 + CO$<br>$\frac{1}{3} FeO \cdot TiO_2 + 2CO = \frac{1}{3} Fe + \frac{1}{3} Ti_2O_3 + 2CO_2$<br>$\frac{1}{3} FeO \cdot TiO_2 + C = \frac{1}{3} Fe + \frac{1}{3} TiO + CO$   | AZ<br>37910-33,887<br>40106-36,387<br>42434-35,877<br>53684-37,827   | (11)                      |
| $FeO \cdot TiO_2 + 4Ti_2O_3 = 3Ti_2O_3 + Fe$<br>$2FeO \cdot TiO_2 + Ti_2O_3 = 3(FeO \cdot 2TiO_3) + Fe$<br>$Fe + Ti + \frac{1}{2} O_2 = FeO \cdot TiO_2$<br>$Fe + 2Ti + 2SO_2 = FeO \cdot 2TiO_3$<br>$Mg + Ti + \frac{1}{2} O_2 = MgO \cdot TiO_2$<br>$Mg + 2Ti + 2SO_2 = MgO \cdot 2TiO_3$<br>$2Ti + 1.5O_2 = Ti_2O_3$<br>$2Ti + 2SO_2 = Ti_2O_3$<br>$2Ti + \frac{1}{2} O_2 = Ti_2O_3$ | AZ <sub>1959-1960</sub><br>-26804+5,87<br>-2680+1,767<br>-26830+1,55,87<br>AZ<br>-507080+84,27<br>AZ <sub>1959-1960</sub><br>-57880+126,17<br>-58320+1297<br>AZ<br>-38800+1807<br>-57808+100,887<br>AZ <sub>1959-1960</sub><br>-168708+207 | [29, p. 64]               |

to 4:1, ilmenite appears in the solid solution, containing up to 10%  $Ti_2O_3$ .

Because of the formation of solid solutions in the ilmenite-titanium sesquioxide system, the reduction processes under real conditions differ substantially from those calculated from thermodynamic data without consideration of solid-solution formation.

It has been established that 1.95% of ilmenite added to  $Ti_2O_3$  is completely dissolved in the titanium sesquioxide lattice, with the result that a single-phase solid solution forms. Use of smaller ilmenite additives results in the formation of  $Ti_3O_5$  and metallic iron [10, page 42].

The reaction of titanium monoxide (TiO) with ilmenite was studied in [29]. The starting materials were natural ilmenite containing no trivalent iron and titanium monoxide containing 96% TiO and 4%  $TiO_2$ . The ilmenite-monoxide ratio was varied from 0.1:1 to 3:1.

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The experiments were conducted in an argon atmosphere at temperatures ranging from 1300 to 1700°C. The completeness of the reaction between the ilmenite and titanium monoxide was determined from the amount of metallic iron in the reaction products.

It was established that the extent of ferrous-oxide reduction declines with rising temperature at all ilmenite-titanium oxide proportions. More of the titanium oxide than the sesquioxide is broken down. Characteristically, as in the case of the reaction between ilmenite and titanium sesquioxide, the reaction does not go to completion owing to the formation of tagirovite and anosovite solid solutions. The authors conclude that with the proportions  $\text{FeO} \cdot \text{TiO}_2 : \text{TiO} < 1:1$ , the reaction proceeds on the scheme



but for  $\text{FeO} \cdot \text{TiO}_2 : \text{TiO} > 1:1$  according to the scheme



It has been reported that the products fuse as the ilmenite-monoxide ratio is increased beyond 1.5:1 - something that was not observed in sesquioxide experiments.

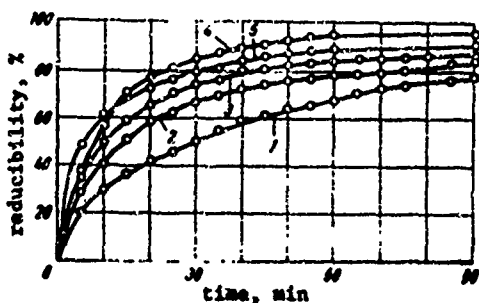


Figure 8. Reducibility of ilmenite concentrate by hydrogen at various temperatures, °C: 1) 800; 2) 900; 3) 1000; 4) 1100; 5) 1200.

These studies indicate that the reduction of ferrous oxide from ilmenite is complicated by the presence of lower titanium

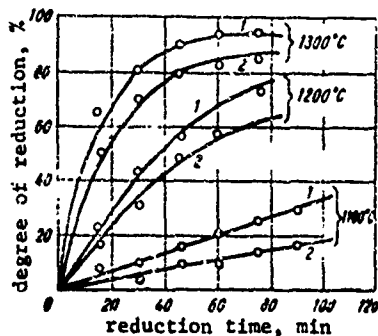


Figure 9. Reducibility of titanium concentrates by solid carbon at various temperatures: 1) ilmenite concentrate; 2) arizonite concentrate.

oxides. As the ferrous oxide content declined in the system, lower titanium oxides accumulated.

V.A. Reznichenko et al. [16] studied the reducibility of ilmenite concentrate. Figure 8 presents data on the reducibility of ilmenite concentrate by hydrogen, while the reducing agent in Fig. 9 is solid carbon. Figure 8 indicates that when hydrogen is the reducer, the best results are obtained at 1100°C. A further rise in temperature inhibits reduction. This inhibition is not observed during reduction by solid agents.

The hydrogen reducibility of a finely ground mechanical mixture of  $Fe_2O_3 + 3TiO_2$  (which corresponds to the composition of arizonite), natural arizonite concentrate, and rutilized ilmenite was studied in [10, page 82]. The results presented in Figs. 10 and 11 indicate that the iron is most easily reduced from the mechanical mixture of  $Fe_2O_3 + 3TiO$  [sic] and that the arizonite concentrate is most difficult to reduce. Reducibility was studied up to 900°C, at which point practically no lower titanium oxides formed and, consequently, solid solutions of ilmenite with these oxides and anosovite could not form. The results obtained by these authors indicate that rutilized ilmenite and the arizonite

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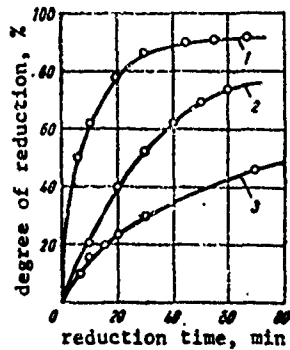


Figure 10. Reducibility of titanium-bearing materials by hydrogen at 700°C. 1) Mixture of  $Fe_2O_3 + 3TiO_2$ ; 2) ilmenite concentrate; 3) arizonite concentrate.

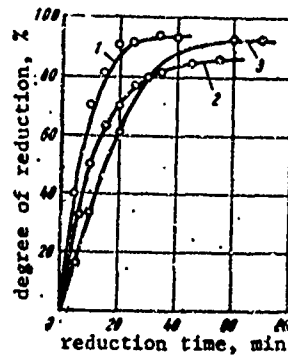


Figure 11. Reducibility of titanium-bearing materials by hydrogen at 900°C. 1) Mixture of  $Fe_2O_3 + 3TiO_2$ ; 2) ilmenite concentrate; 3) arizonite concentrate.

phase are more difficult to reduce than the free ferric oxide.

The same source reports a study of the reducibility of pure ilmenite, rutilized ilmenite, and arizonite concentrates by solid carbon at 1250°C. Bricquettes were made from a mixture of the concentrate and ground petroleum coke, taken in a mass of 10% of that of the concentrate. The material was reduced in a current of argon. The results, which appear in Fig. 12, indicate that the arizonite concentrate is more difficult to reduce than the rutilized ilmenite concentrate.

TABLE 20  
Chemical Composition of Ilmenite Concentrates, %

| concentrate | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $FeO$ | $CaO$ | $MgO$ | $V_2O_5$ |
|-------------|---------|---------|-----------|-----------|-------|-------|-------|----------|
| I           | 2.44    | 44.10   | 1.40      | 7.55      | 40.56 | 1.25  | 2.28  | 0.20     |
| II          | 1.25    | 51.10   | 1.01      | 5.52      | 38.48 | Her   | 0.51  | 0.10     |

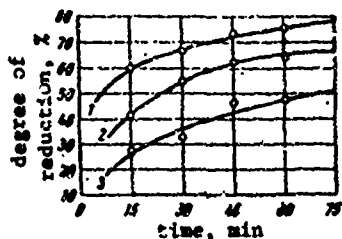
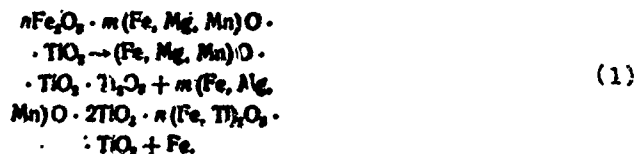


Figure 12. Reducibility of titanium concentrates by solid carbon at 1250°C. 1) Ilmenite concentrate; 2) rutilized ilmenite concentrate; 3) arizonite concentrate.

determined for this process, as follows: temperature 1250 ± 10°C, amount of reducing agent 10% of concentrate mass, furnace tilt angle 1.5°, charging rate 4 kg/h. Under these conditions, the iron oxides were 58-65% reduced.

The authors established that iron and titanium are reduced simultaneously as the temperature is raised. At 1200-1250°C, no ilmenite is found in the reduced product, but there are larger amounts of tagirovite, anosovite, and metallic iron. On the basis of these experiments, the authors submit the following scheme for the reduction of ilmenite at temperatures above 1150°C:



The source cited here [10, page 96] attests to the uniqueness and difficulty of the process in which iron oxides are reduced from ilmenite in the solid phase as compared with the reduction of purely iron-ore minerals.

In [10, page 86], a study was made of the reducibility of unground ilmenite, rutilized, and arizonite concentrates at temperatures from 1000 to 1350°C. The granulometric compositions of

Scaled-up laboratory studies were also carried out to investigate preliminary reduction of ilmenite concentrates in a rotary electric furnace 100 mm in inside diameter and 1.5 m long. Powdered slag and granules were used for the experiments [10, page 96].

The temperature in the reduction zone was varied from 900 to 1250°C. Table 20 shows the compositions of the initial concentrates. Optimum conditions were

the starting concentrates were given on page 82.

It was established that the ilmenite concentrate has the best reducibility at 1200°C, the arizonite concentrate is second, and the rutilized concentrate the most difficult to reduce. This sequence of the concentrates is explained in part by their differing granulometric compositions. The coarser rutilized ilmenite concentrate was reduced more slowly.

It was established that the fineness to which the reducing agent — anthracite — was ground influences concentrate reducibility. Use of fine-ground anthracite (-0.074 mm) in the temperature range from 1000 to 1200°C increases the reducibility of the concentrate by comparison with coarser anthracite (0.25 mm). This difference is levelled at 1300°C. At 1300°C, the reducibility of a briquetted charge is higher than that of a powdered charge.

Interest attaches to the research of M.B. Rapoport and V.M. Kozlov [15]. In these studies, the charge was composed of unground concentrates with anthracite added [13 parts (by mass) for the ilmenite concentrates and 9.5 parts (by mass) for the arizonite concentrates]. The charge was briquetted under a pressure of 800 kgf/cm<sup>2</sup> after addition of 6% of sulfite liquor. Briquettes 30 mm in diameter and 20-25 mm high were formed. After drying, they were placed in a graphite crucible under an anthracite blanket. The crucible with the briquettes was placed in a furnace that had been preheated to 1000-1300°C.

(1)

TABLE 21  
Degree of Reduction of Iron and Titanium Oxides from  
Titanium Concentrates

| tempera-<br>ture, °C | degree of oxide reduction, % |                  |                       |                  |           |                  |
|----------------------|------------------------------|------------------|-----------------------|------------------|-----------|------------------|
|                      | ilmenite                     |                  | rutilized<br>ilmenite |                  | arizonite |                  |
|                      | FeO                          | TiO <sub>2</sub> | FeO                   | TiO <sub>2</sub> | FeO       | TiO <sub>2</sub> |
| 1000                 | 2.55                         | 0                | 2.85                  | 0                | 7.45      | 0                |
| 1100                 | 45.4                         | 33.6             | 34.7                  | 32.2             | 45.5      | 32.1             |
| 1200                 | 77.0                         | 68.6             | 67.9                  | 78.0             | 75.0      | 74.3             |
| 1300                 | 82.1                         | 76.2             | 83.8                  | 84.2             | 80.3      | 81.5             |
| 1350                 | 86.5                         | 72.7             | 78.4                  | 81.7             | 83.8      | 80.3             |

The  $Fe_{tot}$ ,  $Fe_{met}$ ,  $Ti_{tot}$ ,  $Ti^{2+}$ , and  $Ti^{3+}$  in the final final product were determined. The results of these experiments appear in Table 21. This table shows that reduction of ferrous oxide at temperatures above 1000°C is accompanied by simultaneous reduction of the titanium dioxide to a lower oxidation state. At temperatures above 1300°C, on the other hand, the reducibility of the charge declines because of the onset of sintering and formation of tagirovite and anosovite solid solutions.

The reduction of titanium dioxide by carbon (calcined petroleum coke) mixed with hydrogen-reduced metallic iron, alumina concentrated by acid washing, quartz sand, chemically pure calcium oxide, and metallic silicon as additives was investigated in [30].

It was found that the reaction of  $TiO_2$  with carbon begins at about 950°C. At 1800°C, reduction proceeds to the formation of a  $TiO-TiC$  solid solution. Reduction is more complete in the presence of iron and in the 1600-1800°C temperature range all of the titanium is converted to  $TiC$  or, more probably, to  $TiCN$ . The  $Al_2O_3$  additive promotes more complete reduction. Silica, calcium oxide, and silicon have no discernible influence on  $TiO_2$  reduction.

It has been established by O.A. Yesin, P.V. Gel'd [31, 32] and other investigators that the slowest stage, that which determines the rate of the iron-oxide-reduction process at high temperatures, is the gasification reaction of carbon:



The carbon monoxide formed in this reaction is the basic reducing agent in this particular system.

Z.F. Chukhanov [25, page 164] indicates that it is impossible to bring about a state of the process in industrial furnaces such that the reaction rate would be high enough to cause all of the  $CO_2$  to interact with carbon to form carbon monoxide, and for this reaction to be independent of coke activity. According to Z.F. Chukhanov's calculations, this would require a temperature above 2000°C.

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It has been established that the reduction reactions are accelerated in the presence of alkali-metal salts and mineral oxides. This is because the metals in these additives are capable of penetrating into the carbon lattice, deforming it, and thereby enhancing its chemical activity.

Addition of alkali- and alkaline-earth-metal salts accelerates the reduction of ilmenite in the solid phase. This was established by E.V. Britske et al. [33], O.A. Eysin and P.V. Gel'd [32], and G.I. Chufarov [25]. E.V. Britske found that the addition of  $K_2O$  in an amount equal to 10% of charge mass accelerates the reduction process by a factor of 5-10. G.I. Chufarov et al. determined that a potash additive accelerates the reduction of ilmenite by carbon monoxide in the presence of carbon at  $1050^\circ C$  by a factor of 8-9, while carbon monoxide alone accelerates it only by 1.5-2 times. This indicates that the above additives accelerate gasification of the carbon, lowering the carbon dioxide partial pressure and raising that of the monoxide. It is this that accelerates the reduction processes.

The effects of soda, calcium carbonate, and magnesium carbonate on the reduction of arizonite concentrate at various temperatures were studied in [10, page 86]. It was found that reduction is accelerated by addition of soda only up to a content of 3%. Increasing the soda additive above 3% does not accelerate the reduction of ferrous oxide. Sodium chloride has a similar effect. Calcium and magnesium carbonate additives inhibit reduction.

Reduction of ferrous oxide in the molten slag is an important factor in the smelting of rich titanium slags, just as it is in iron smelting [34, 35].

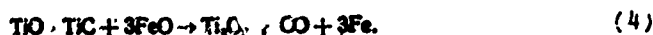
It has been established that when a charge consisting of titanium concentrate and a reducing agent is melted — even at temperatures of  $1350-1400^\circ C$  — the ferrous oxide and titanium oxides are reduced only to an insignificant degree in the solid phases. Most of the reduction of the ferrous oxide takes place in the molten slag. As we noted earlier,  $Ti_2O_3$  and  $TiO$  accumulate in the slag as the iron is reduced from its lower oxide. The

contents of FeO, TiO<sub>2</sub>, Ti<sub>2</sub>O<sub>3</sub>, and TiO in the slag are interrelated and determined by the equilibrium conditions established in this process.

To ascertain the mechanism by which ferrous oxide is reduced in thermal smelting of the ores, it will be necessary to dwell on the behavior of titanium carbide in this process. We know that there is practically no reduction of titanium oxides to the metal by carbon, because titanium carbide, which is a stable compound, is formed at high temperatures instead of metallic titanium. When ferrous oxide is present in the slag, the titanium carbide reacts with it as follows:



Since titanium oxycarbide (TiO·TIC) is present in the slag, another possible reaction is



Thus, ferrous oxide can be reduced from the slag not only with solid carbon, but also with titanium carbide, which forms at temperatures above 1600°C (formation of titanium oxycarbonitrides is also possible). Since carbon monoxide is formed in all of these reactions, vigorous bumping of the vat facilitates contact between the solid carbon, the slag, and the iron.

TABLE 22  
Losses of Calcium Oxide and Magnesium Oxide During Smelting

| charge                                  | CaO, %                 |                 |                        | MgO, %                 |                 |                        |
|---|------------------------|-----------------|------------------------|------------------------|-----------------|------------------------|
|   | content in concentrate | content in slag | losses during smelting | content in concentrate | content in slag | losses during smelting |
| powdered . . . . .                      | 5.2                    | 2.8             | 44                     | 1.28                   | 1.76            | 11                     |
| mixed with limestone additive . . . . . | 8.0                    | 8.0             | 10                     | 1.31                   | 1.66            | 15                     |

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The possibility of activation of the ferrous-oxide reduction when calcium and magnesium oxides are present in the slag should be borne in mind. Table 22 gives data on the losses of calcium oxide and magnesium oxide during smelting, as calculated from material-balance results [16].

From the above, and from the data given in Table 22, we see that the losses of silicon, calcium, and magnesium are several times greater than those of titanium and iron. It is demonstrated in [25, page 126] that calcium is reduced to metallic calcium vapor with subsequent formation of calcium carbide. Naturally, a certain fraction of the calcium vapor escapes from the furnace with the current of reducing gas and is oxidized outside the melt to finely dispersed calcium oxide.

TABLE 23  
Distribution of Silicon in Smelting Products [16]

| charge   | Given silicon with concentrate |       | silicon obtained in slag |       | silicon ex-traction into slag, % | sil' con loss, % | silicon ex-traction into pig, % |
|--|--------------------------------|-------|--------------------------|-------|----------------------------------|------------------|---------------------------------|
|  | %                              | kg    | %                        | kg    |                                  |                  |                                 |
| combined (75% briquettes, 25% powder charge) . . . . . | 2,05                           | 3496  | 2,35                     | 2085  | 62                               | 17,83            | 0,18                            |
| powder . . . . .                                       | 2,05                           | 3454  | 1,8                      | 1961  | 87                               | 42,79            | 0,21                            |
| mixed (60% briquettes, 40% powdered charge) . . . . .  | 2,13                           | 19777 | 2,31                     | 14857 | 74                               | 25,77            | 0,23                            |
| mixed . . . . .  | 2,65                           | 2138  | —                        | —     | 72,1                             | 16,1             | 11,8                            |

Magnesium oxide present in the slag can also be reduced to metallic magnesium, which transfers to the vapor phase. The reduction of magnesium oxide to the metal can also occur on interaction of MgO with titanium carbide, according to the reaction [2]



The formation of calcium and magnesium vapor helps accelerate the reduction of iron oxides from the molten slag.

It follows from the survey given above that the reduction of ferrous oxide from liquid slags during smelting of ilmenite concentrates in an electric furnace can take place at a high rate, and this is observed in practice. This point is of great importance for intensification of the smelting process. There is no need for the smelting to wait for a slow stage in which iron is reduced in the solid phase; it is recommended that its reduction be forced directly in the liquid slag. This peculiarity of ferrous-oxide reduction forms the basis for a fluxless method of smelting ilmenite concentrate to rich titanium slag.<sup>(2)</sup>

Silica reduction processes are an important factor in thermal ore smelting. Like carbon, silicon is a very strong reducer of silicon dioxide to the monoxide. Silicon reduces SiO<sub>2</sub> more rapidly than does carbon.

Under these conditions, the reduction of SiO<sub>2</sub> by silicon can be represented by the scheme



These reactions result in considerable depletion of silicon monoxide from the melt during smelting.

Pig iron contains 0.36-0.7% silicon. Table shows its distribution among the smelting products. While 95-96% of the titanium dioxide is extracted into the slag, the figure is only 57-82% for silicon dioxide. This is a result of rapid depletion of the monoxide from the furnace because of its high volatility.

#### The Role of Titanium Oxides in the Electrothermal Process

Data were given above to indicate that the reduction of iron oxides from titanium concentrates is accompanied at temperatures above 1000-1100°C by simultaneous reduction of the titanium dioxide to lower oxides. The latter determine the electrical conductivity, viscosity, and other properties of the titanium slags. It is therefore necessary to devote special consideration to the properties of titanium oxides and to the lower oxides in particu-

<sup>e</sup> (2) appears on page 109.  
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There are now more than ten known oxides in which titanium occurs in its di-, tri-, and quadrivalent states. The lack of an explicit phase diagram that has adequate experimental support for the Ti-TiO<sub>2</sub> system [36] makes it difficult to investigate the products of metallurgical titanium-concentrate processing. Only the region of the diagram between Ti and the compound Ti<sub>2</sub>O<sub>3</sub> has been studied in detail.

According to [37], the Ti-TiO<sub>2</sub> system has intermediate stable states, and, in particular, a series of compounds with the general formula Ti<sub>n</sub>O<sub>2n-1</sub>.

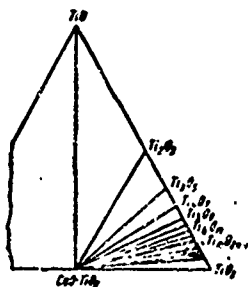


Figure 13. Phase diagram of CaO-TiO-TiO<sub>2</sub> system [54].

It was established in [10, page 278] in a study of an artificially prepared slag containing 21% CaO and 79% TiO<sub>2</sub> that the compound CaO·TiO<sub>2</sub> (perovskite) was invariably present in the slag at various stages of reduction, and that the excess titanium dioxide was reduced as though it were in the free stage. The titanium oxide compositions found here are given below as functions of reduction time in a Kryptol furnace at 1440°C.

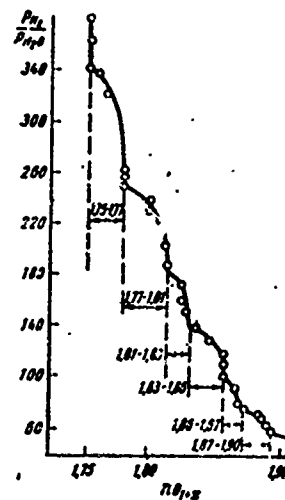


Figure 14. Equilibrium gas compositions in reduction of pure titanium dioxide by hydrogen at 1000-1100°C.

|                    |  |
|--------------------|--|
| time, h            |  |
| 1.4                | ..... TiO <sub>n</sub> -Ti <sub>n</sub> O <sub>2n-1</sub> (n = 6-10) |
| 1                  | ..... TiO <sub>2</sub>   |
| 2                  | ..... TiO <sub>2</sub> , Ti <sub>2</sub> O <sub>3</sub>              |
| 4                  | ..... TiO <sub>2</sub>   |
| 8                  | ..... TiO <sub>2</sub> , Ti <sub>2</sub> O <sub>3</sub>              |
| 8                  | ..... TiO <sub>2</sub> , Ti <sub>2</sub> O <sub>3</sub>              |
| completely reduced | ..... Ti <sub>2</sub> O <sub>3</sub> , Ti                            |
| slag.....          | ..... Ti(O, C)   |

Figure 13 reproduces the triangulation of the ternary CaO-TiO-TiO<sub>2</sub> system [41].

Reference [38] studied phase relationships in the TiO<sub>2</sub>-Ti<sub>1.75</sub> system, i.e., in the region in which Andersson [37] used x-ray diffraction analysis to establish the existence of a homologous series of oxides with the general formula Ti<sub>n</sub>O<sub>2n-1</sub>, where n = 4, 5...10 (TiO<sub>1.75</sub>, TiO<sub>1.80</sub>, TiO<sub>1.833</sub>, TiO<sub>1.858</sub>, TiO<sub>1.873</sub>, TiO<sub>1.889</sub>, TiO<sub>1.90</sub>).

Highly purified titanium dioxide was used to investigate the equilibrium of titanium oxides with H<sub>2</sub>/H<sub>2</sub>O mixtures. The tests were made at a temperature of about 1000°C, since no equilibrium states were reached below that temperature. It was established that hydrogen reduction proceeds only as far as the oxide of the approximate composition TiO<sub>1.75</sub> at 1000-1100°C. Equilibrium was established after 3-4 hours at 1030°C, and much later in oxidation.

The results of these experiments appear in Fig. 14, from which we see that six phases of variable composition exist at high temperature in the TiO<sub>1.75</sub>-1.90 interval: TiO<sub>1.87-1.90</sub>, TiO<sub>1.86-1.87</sub>, TiO<sub>1.83-1.86</sub>, TiO<sub>1.81-1.83</sub>, TiO<sub>1.77-1.81</sub>, TiO<sub>1.75-1.77</sub>.

Titanium Dioxide TiO<sub>2</sub>

Pure titanium dioxide is white in color and has a density in the range from 3.9 to 4.25. It is one of the most stable oxides of titanium found in nature in the pure form. The density of TiO<sub>2</sub> increases with calcining temperature. It is 3.89-3.95 at 600°C, 4.15 at 800°C, and 4.25 at 1000-1200°C. The melting point of

All weak requires Fig. tant sys However, work is of TiO<sub>2</sub> tri- and Titanium TiO [24, pag type. Its melt Sev monoxide

TiO<sub>2</sub> is 1840 ± 10°C.

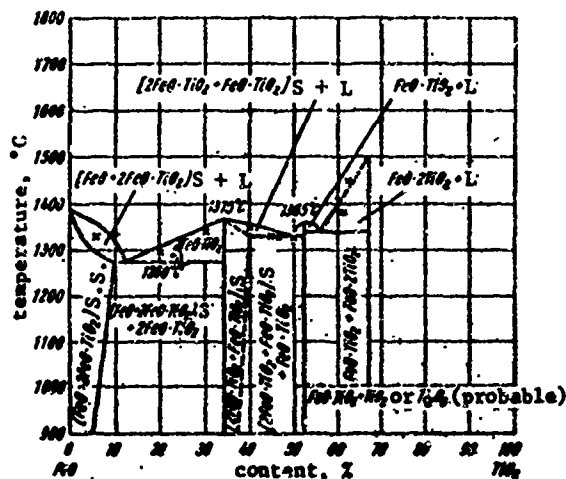


Figure 15. Phase diagram of FeO-TiO<sub>2</sub> system.

Although titanium dioxide is a dielectric, even in a weak reducing environment it loses some of its oxygen and acquires electronic conductivity.

Figures 15-21 present fusibility curves of the most important systems containing TiO<sub>2</sub> that are encountered during smelting. However, it must be remembered that practical high-temperature work is done not with pure titanium dioxide, but with a mixture of TiO<sub>2</sub> with the lower oxides, in which the titanium is in the tri- and divalent states.

#### Titanium Monoxide TiO

Titanium monoxide is stable in the TiO<sub>0.60</sub>-TiO<sub>1.25</sub> interval [24, page 64] and crystallizes in a cubic lattice of the NaCl type. Its density varies in the range from 4.88 to 6.00 g/cm<sup>2</sup>. Its melting point is 2020°C.

Several methods are known for the acquisition of titanium monoxide: reduction of titanium dioxide by carbon in a vacuum,

reduction of titanium dioxide in a vacuum by reducing metals (Mg, Zn, TiC, Ti), etc.

Reduction of titanium dioxide with wood charcoal at atmospheric pressure and temperatures in the range from 1100 to 1500°C results in a solution of the monoxide and titanium carbide with 33 to 60% TiC [39]. In [24, page 64], titanium monoxide was prepared by the reaction



In this case, a mixture of  $\text{TiO}_2$  with titanium in briquette form was held for 2 hours at 1550°C in a vacuum induction furnace. The coarse-grained product had a yellowish-gold color. Microstructural analysis detected only a single phase —  $\text{TiO}$  — in the form of large crystals. When it was oxidized to constant mass at 1000°C, the weight gain was about 24%, or near the theoretical gain for oxidation to  $\text{TiO}_2$ .

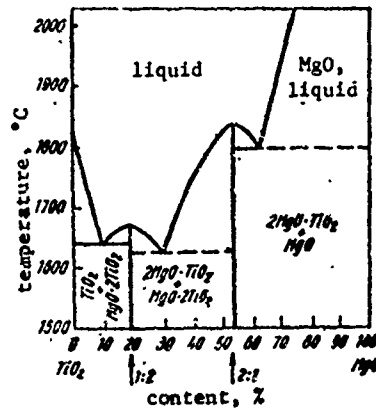


Figure 16. Phase diagram of  $\text{TiO}_2$ - $\text{MgO}$  system.

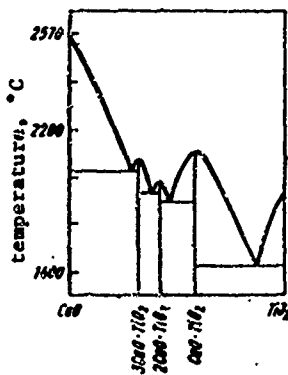


Figure 17. Phase diagram of  $\text{CaO}$ - $\text{TiO}_2$  system.

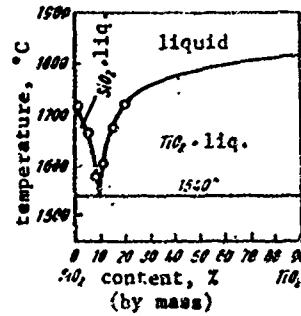


Figure 18. Phase diagram of  $\text{SiO}_2$ - $\text{TiO}_2$  system.

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Other methods of preparing titanium monoxide do not yield the pure product.

A characteristic property of titanium monoxide is its ability at high temperatures to form a continuous series of solid solutions of the  $Ti(O, C)$  type [40], which may also include  $TiN$  [41].  $TiN$  is most stable up to  $1600^{\circ}C$ . At higher temperatures, the titanium carbide content increases, and at  $1900^{\circ}C$ , titanium monoxide has been fully converted to titanium carbide.

It is reported in [42] that the  $Ti(O, C)$  solid solution is detected not in the final slags, when the metal and slag have been separated, but in individual nonequilibrium zones of the primary slag melt that have been saturated with beads of metal and unreacted coke.

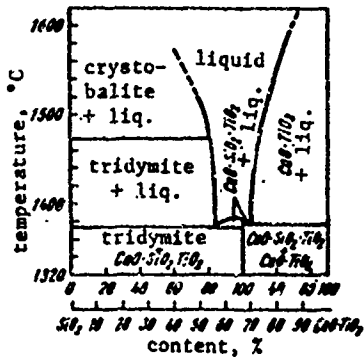


Figure 19. Phase diagram of  $CaO \cdot TiO_2 - SiO_2$  system.

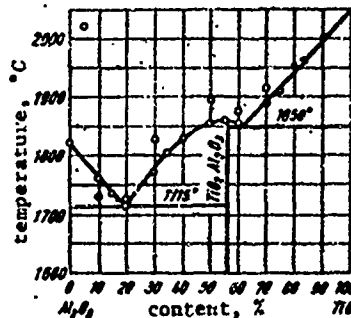


Figure 20. Phase diagram of  $Al_2O_3 - TiO_2$  system.

It was established in [42] that compounds with oxygen contents lower than that of  $TiO$  ( $Ti_2O$  and  $Ti_3O_2$ ) do not occur in these slags. It is reported that the compound  $Ti_3O_2$  is highly volatile in a vacuum at  $1100^{\circ}C$ .

According to [43], titanium dioxide is reduced to the monoxide and carbide according to the scheme



In the last stage, the titanium monoxide forms a solid solution with titanium carbide and, according to [40], the chemical

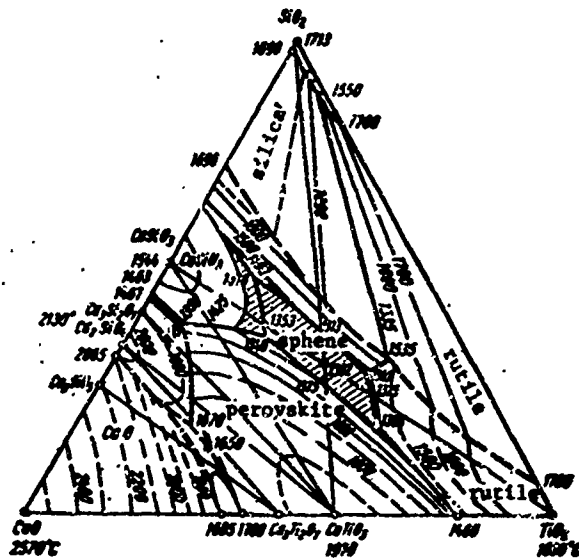


Figure 21. Phase diagram of CaO-SiO<sub>2</sub>-TiO<sub>2</sub> system.

composition of this solution can be stated as Ti(O, C). A.V. Rudneva [42] also notes that a continuous series of solid solutions of this type forms at the last stage of reduction.

Titanium monoxide reacts vigorously with ilmenite, but this interaction does not go to completion and diminishes with rising temperatures (Fig. 22).

#### Titanium Sesquioxide Ti<sub>2</sub>O<sub>3</sub>

Titanium sesquioxide is stable in the range from TiO<sub>1.45</sub> to TiO<sub>1.56</sub>. It crystallizes in a lattice of the α-corundum type. Several methods of preparing Ti<sub>2</sub>O<sub>3</sub> are known [24, page 64]:

reduction of titanium dioxide by carbon at 1400°C with 20 hours' holding;

hydrogen reduction of titanium dioxide at 1000-1200°C with 3 hours of holding, or hydrogen reduction with passage of titanium tetrachloride over the dioxide at 650°C;

reduction of titanium dioxide by calcium and magnesium at 1200°C;

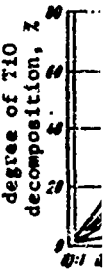


Figure 2. Position of decomposition by ilmenite at 1400°C; 4) 1500°C; 5) 1700°C.

wer: heat is inadequate above 1500°C, ranging from 10.8% TiO<sub>2</sub>. The product, in [10, 11]

Ti<sub>2</sub>O<sub>3</sub> dissolves in TiO<sub>2</sub>, which is iron.

Titania content of 1% and the melting point exceed 50% concentration from 47% the lowest

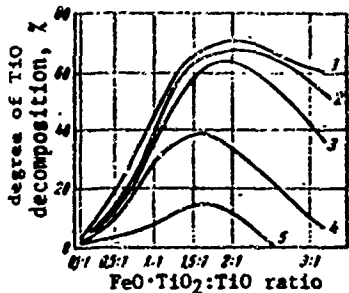


Figure 22. Degree of decomposition of titanium monoxide by ilmenite. 1) 1300°C; 2) 1400°C; 3) 1500°C; 4) 1600°C; 5) 1700°C.

reduction of titanium dioxide by magnesium in a hydrogen atmosphere at 750-800°C;

reduction of titanium dioxide by titanium carbide in an inert atmosphere at 1000-1200°C;

by heating mixtures of MgO + TiC, ZnO + TiC, and CaO + TiC at 1000-1200°C in an inert atmosphere;

reduction of titanium dioxide by metallic titanium in a vacuum.

This last method was used in [24, page 64], in which briquettes

were heated to 1400-1550°C. It was found that heating to 1550°C is inadequate for complete reduction of Ti<sub>2</sub>O<sub>3</sub>. At temperatures above 1550°C, a single phase is obtained in the product: crystals ranging from pink to orange in color. The oxidation weight gain was 10.8%, which is close to theory for the oxidation of Ti<sub>2</sub>O<sub>3</sub> to TiO<sub>2</sub>. The product contained an oxygen excess. To obtain a purer product, the charge was prepared with a deficiency (~7%) of TiO<sub>2</sub> in [10, page 42].

Ti<sub>2</sub>O<sub>3</sub> exhibits basic properties. At high temperatures, it dissolves ilmenite, forming the minerals tagirovite and anosovite [10, pages 42, 28, 29]. Titanium sesquioxide was detected by T.S. Belyakin and V.V. Lapin [44, 45] in slags containing 25.79-14.30% TiO<sub>2</sub>, which had been obtained in smelting of high-titanium pig iron.

Titanium sesquioxide exerts a strong influence on the properties of titanium slags. When the ferrous oxide content is small and the Ti<sub>2</sub>O<sub>3</sub>:TiO<sub>2</sub> ratio does not exceed :.75, it lowers the melting point of the slag. When the ferrous oxide content does not exceed 5%, stable rich titanium slags are obtained in the Ti<sub>2</sub>O<sub>3</sub> concentration range from 0 to 45% at titanium dioxide contents from 47 to 82% [46]. Slags with Ti<sub>2</sub>O<sub>3</sub>:TiO<sub>2</sub> ratios of 0.6-0.8 have the lowest viscosities at ferrous oxide contents below 10%.

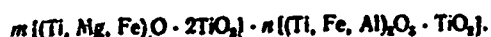
### The Oxide $Ti_3O_5$

The oxide  $Ti_3O_5$  has a rhombic structure. It has been reported stable in the concentration range from  $TiO_{1.7}$  to  $TiO_{1.8}$ . In [24, page 64],  $Ti_3O_5$  was obtained by reducing  $TiO_2$  with carbon and metallic titanium at 1200-1600°C with a holding time of 4-8 hours, and by the reaction between the oxide  $TiO + 2TiO_2$  and  $Ti_2O_3 + TiO_2$  at 1420°C. Another modification with a higher oxygen content than  $Ti_3O_5$  was obtained by reacting titanium dioxide with carbon and titanium.

The oxide  $Ti_3O_5$  is the base of a mineral detected in titanium slags — anosovite. F.V. Syromyatnikov originally gave the name "calcined rutile" to anosovite [47]. E.V. Britske et al. referred to it as "reduced rutile" or the "black mineral" [33]. K.Kh. Tagirov later named it anosovite in honor of the noted Russian metallurgist P.P. Anosov [48, 49]. It was established by x-ray analysis in [50] that anosovite has a rhombic structure and a formula of the  $Me_3O_5$  type.

In 1951, D. . . Belyankin and V.V. Lapin [49] isolated anosovite from a titanium slag containing 30 to 64% of  $TiO_2$  and determined its chemical composition. The authors reported composition inconstancy of anosovite resulting from solid-solution formation. According to [52], anosovite may be given the formula  $Ti_2O_3 \cdot TiO_2$  or  $TiO \cdot 2TiO_2$ , because of the possibility of mutual solution of compounds of the  $MeO \cdot 2TiO_2$  and  $Me_2O_3 \cdot TiO_2$  types.

Thus, anosovite is a solid solution based on the high-temperature modification of the oxide  $Ti_3O_5$ . According to [42, 52], the composition of anosovite can be described by the formula



In addition to the high-temperature modification,  $Ti_3O_5$  also has a low-temperature modification, which crystallizes in the form of short prismatic crystals.

### The Oxide $Ti_5O_9$

An oxide of this composition was investigated in [4, page 21]. The concentration range in which this dark blue phase exists was

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established:  $TiO_{1.82}-TiO_{1.70}$ . This oxide had previously been given the formula  $3Ti_2O_3-4TiO_2$  [53]; in [24, page 64] it was ascribed the formula  $Ti_6O_{11}$ . According to Anderson [37], there are two oxides in this interval:  $Ti_5O_9$  and  $Ti_4O_7$ . If we take the percentage reduction of titanium dioxide to  $Ti_3O_5$  as 100, the composition of the oxide  $Ti_5O_9$  is obtained at 60-70% reduction of  $TiO_2$ .

According to [42], the compound  $Ti_5O_9$  is absent from systems containing ions that substitute  $Ti^{2+}$  and  $Ti^{3+}$  (as is the case in real slags).

#### Opaque Rutile

Opaque rutile is a solution of  $Ti_2O_3$  in  $TiO_2$  that is formed in the initial phase of titanium dioxide reduction [54]. Unlike rutile, crystals of this solution are totally opaque. The concentration range in which opaque rutile exists varies from  $TiO_{1.90}$  to  $TiO_2$ . At  $TiO_{1.90}$ , the  $Ti_2O_3$  content in the solution is 20%.

A monomineral aggregate of opaque rutile is found in slags of the  $TiO_2-Ti_2O_3$  system containing 80 to 98%  $TiO_2$ . In slags of more complex titanium-oxide-content composition, opaque rutile is invariably accompanied by anosovite crystals, while the compound  $Ti_6O_{11}$  is not formed at all. In the  $TiO_2-Ti_2O_3-FeO$  slag system, even at small  $Ti_2O_3$  contents, two phases are observed: opaque rutile and anosovite. No solid solutions based on the  $TiO_2$  structure have been observed in slags produced under industrial conditions in the presence of  $Fe^{2+}$ ,  $Mg^{2+}$ ,  $Al^{3+}$ , and  $Ti^{3+}$  ions. This also applies to the homogeneous series of structurally interrelated compounds with the general formula  $Ti_nO_{2n-1}$ .

Nevertheless, the opaque-rutile structure is obviously individualized in the smelting of slags that have very high titanium dioxide contents.

Footnotes

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<sup>1</sup>See page 107.

99

<sup>2</sup>V.Yu. Kramnik et al. Author's certificate (USSR), No. 119,678, 1959.

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Symbol List

| Manu-<br>script<br>page | Russian | When<br>Typed | Meaning  |
|-------------------------|---------|---------------|----------|
| 90                      | мет     | met           | metallic |
| 95                      | общ     | tot           | total    |
| 99                      | тв      | tv            | solid    |
| 99                      | газ     | gaz           | gas      |

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## Chapter 8

### PRODUCTION TECHNOLOGY OF TITANIUM SLAGS

#### Basic Requirements Made of Titanium Slags

The quality of a titanium slag is determined by its titanium dioxide content and impurity composition. Slags used in the production of titanium tetrachloride must have titanium dioxide contents approaching that of rutile, i.e., they must contain more than 80%  $TiO_2$ . They must also contain minimal amounts of aluminum oxide (no more than 1.5%) and ferrous oxide (no more than 3%). This is because a major part of the aluminum chlorides and ferris chloride condenses together with the titanium tetrachloride during chlorination of the vapor-gas mixture, forming a suspension that does not readily settle. The slag may not contain large amounts of manganese, chromium, or magnesium oxides, silicon dioxide, etc. The smaller the amount of impurities in the slag, the higher the economy of the process. Impurity-free slags make it possible to increase equipment productivity and titanium extraction yield at the chlorination and purification stages and to obtain high-quality sponge titanium from the more thoroughly purified titanium tetrachloride.

A slag used in the production of pigment titanium dioxide by the sulfuric acid method may contain no more than 0.3% chromic oxide, but ferrous oxide contents up to 9-12% are permissible.

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There are two known methods of smelting titanium concentrates for titanium-rich slags: intermittent and continuous. As the name implies, the intermittent method is characterized by charging of the furnace with enough slag to fill the entire furnace space. After reduction of the ferrous oxide to the content specified for the slag, the smelting products are discharged from the furnace. The cycle is then repeated.

In the continuous method of slag smelting, fresh charge is injected continuously or at frequent intervals. The slag and pig iron are removed from the furnace periodically as they accumulate.

The intermittent process is characterized by the following features:

- 1) the possibility of refining the slag to a low ferrous oxide content;
- 2) the possibility of quick fusion of the charge to produce a slag containing 10-20% ferrous oxide, which is subsequently reduced from the molten slag. The slag produced during the melting phase has a low melting point and the transition to the high-temperature-melt phase occurs only as the slag is refined; this helps reduce heat losses and improve furnace productivity;
- 3) the possibility of producing slags with high titanium contents, ranging up to 90-92% converted to the dioxide.

The characteristics of the continuous method differ:

a) owing to the absence of the slag-refining phase, the furnace temperature must be constant and quite high; under these conditions, slag fusibility is ensured either by retaining a high ferrous oxide content in the slag or by injecting a flux, such as limestone, into the charge;

b) a reducing agent is injected into the charge immediately in the amount that ensures acquisition of a slag of the desired composition. This eliminates the possibility of rapid charge fusion, and much of the reduction process takes place in the solid phase.

There are several varieties of the continuous and intermittent smelting methods, including: smelting with and without fluxing additives, smelting of briquetted, unriquetted, and mixed charges, agglomerated-charge smelting, and the so-called two-stage smelting process.

#### The Thermal Ore Furnace and Preparations for Smelting

In principle, titanium concentrates can be smelted in thermal ore furnaces of any construction. The furnaces may be stationary or rotary, with closed or open tops. Stationary furnaces are usually built for high productivity, while the rotary furnaces are made in comparatively small sizes. Closed-top furnaces are preferred, since they make it possible to utilize the flue gas that forms and improve working conditions.

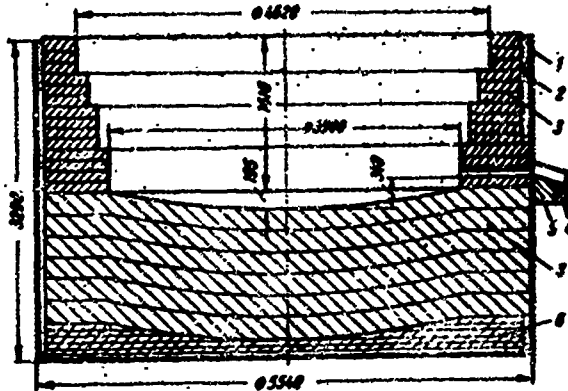


Figure 23. Diagram of shaft brickwork of thermal ore furnace. 1) asbestos sheet; 2) magnesite grit; 3) Mg1-3 magnesite; 4) graphite block; 5) fireclay; 6) Mg1 magnesite.

The design elements of a thermal ore furnace for smelting titanium-rich slags are practically the same as those of similar furnace designs used to smelt out ferroalloys. It will therefore be convenient to limit the description to the design and operating mode of the Soviet 5090-kVA stationary open-top furnace [10, page 105]. This furnace consists of a foundation, a shell, a bottom, machinery for loading the charge and tapping the pig iron and slag

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electrode devices, secondary-circuit wires, and cooling and ventilation systems.

Steel I-beams are laid on the furnace foundation, and covered with steel slabs, which support the bottom and shell of the furnace. Air circulates freely between the steel beams, helping to cool the bottom.

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The cylindrical steel shell of the furnace, which is 5.5 m in diameter, is made from two welded-up halves. The shell is lined with magnesite brick on the inside. Special attention is given to high-quality lining work on the furnace in the zone in which the pig iron accumulates (a diagram of the furnace brickwork appears in Fig. 23). The pig-iron pool ranges up to 1 m deep. It is strongly overheated owing to the large difference between the slag and pig-iron melting points.

The brickwork is particularly liable to damage at the interface between the pig iron and the slag. It must therefore be of very high quality. To prevent damage to the brickwork in this zone, molten charge is allowed to harden into a lining on its surface.

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In contrast to the furnaces used to smelt ferroalloys, carbon blocks are not used to line the furnace walls and bottom. This is because smelting of titanium slags forms a pig iron with a low carbon content that dissolves carbon readily and quickly erodes carbon liners [55]. The chemical activity of the pig iron is also determined by the presence of a certain amount of titanium in it, apparently in the form of the carbide, which reacts with lining oxides and reduces them [56]. In practice, therefore, an effort is made to prevent contact between the overheated pig iron and the furnace lining, especially at the interface. A deep pool of pig iron is maintained to protect the bottom; here it is necessary that a layer of metal freeze at the bottom of the pool.

The furnace shaft is 0.4 m in diameter and 1.6 m high. The walls are staggered upward as indicated in Fig. 23. The tap hole is 310 mm above the lowest point of the bottom, which takes the form of an inverted vault with a sagitta of 195 mm. The furnace

walls, which are about 700 mm thick, rest on a bottom 1.4 m high. The space between the furnace walls and shell (70-100 mm) is filled with magnesite grit, which takes up the thermal forces that arise as the brickwork expands. The furnace tap hole is provided with a shunt unit for electrical heating out.

The charging unit is mounted above the top of the furnace and consists of three hoppers with jaw-type gates through which the charge material is fed into the furnace via rotary chutes that make it possible to aim the charge at the desired spot in the furnace. The gases escape through an exhaust hood.

A newly lined furnace can be used for slag smelting only after thorough drying, baking out, and slag-liner buildup.

The brickwork is dried for 4-5 days by a wood fire or resistance furnace on the furnace bottom. During this process, the furnace shaft is closed at the top to retain the heat.

When drying is complete, the brickwork is baked out with current supplied through graphitized electrodes. To protect the furnace bottom from arcing, a stack of magnesite bricks is placed under each electrode. Coke is loaded into the furnace to form a layer at least 0.5 m deep. Current is then switched to the electrodes and the load is progressively increased in accordance with a special diagram. The current is switched off at intervals to allow equalization of temperature through the entire brickwork. The burned-out coke is replenished at intervals to keep the bed depth constant. After the refractory brick has been baked out, the next step is building up a liner on the furnace walls. A 6-8-ton charge is loaded into the furnace for this purpose. The charge is a conical heap that covers the bottom of the furnace to a distance of about 0.5 m from the walls. The electrodes are lowered and the charge begins to melt. When a slag melt has formed in the zone between the electrodes, 100-150 kg of anthracite are loaded into it, with the result that the melt boils up, fills the remaining space between the cone and furnace walls, and freezes in this space to form the liner. This liner is more refractory than the slag, since it is formed with an excess of

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carbon in the charge and therefore does not melt through under normal smelting temperature conditions.

The unsolidified melt is released from the furnace and another charge is loaded to repeat the lining-buildup operation until the lining has reached the top of the furnace walls. When the lining is built up in this way, about 40 tons of charge and up to 50 thousand kWh of electric power are used for a shaft 4 meters in diameter.

If the condition of the liner is watched carefully and its thickness is maintained, the furnace can be used for more than 2000 melts before relining.

Type ETTsPT 7500/6m transformers with five voltage stages: 133.5, 118, 106, 96.5, and 89 V are used to supply electric current to the furnace. The transformer windings are delta-connected and provided with forced oil cooling. The amperage to the furnace is held constant, and the voltage stages are maintained by means of relay-contactor automatic controllers. The voltage stages are selected with the furnace off.

The furnace uses graphitized electrodes 500-610 mm in diameter, which are held in four-jaw ring-type electrode holders suspended from traverses that are raised and lowered by electric winches. The electrodes have a resistivity of  $8-14 \Omega \cdot \text{mm}^2 \cdot \text{m}^{-1}$  and an apparent density of  $1.6-1.8 \text{ g/cm}^3$ . The permissible current density is  $12-30 \text{ A/cm}^2$ .

Self-annealing electrodes have come into extensive use in thermal ore furnaces. They are the only ones possible in high-power furnaces, which require electrodes 900-1100 mm in diameter.

In the furnace design being described here, the graphitized electrode consists of several parts, between which electrical contact is established by screwing one part of the electrode into another. Hence the end surfaces of the electrodes must be fitted very carefully. The tightness of the contact joint is checked with a feeler gauge — a steel plate 0.25 mm thick. In changing electrodes, the electrodes may not be clamped at the point of the graft.

Suspension-type electrode holders are generally used for thermal ore furnaces. However, cantilevered electrode holders are also encountered. The most critical part of an electrode holder is the electrode clamp, which must ensure good electrical contact between the electrode and the current-conducting jaws and hold the electrode firmly. It must have good magnetic insulation to reduce electrical losses and heating of the ring by induction currents, and must be reliably insulated from the contact jaws.

As a result of periodic electrode changes, the contact joint is continuously being broken, and this complicates operation of the furnace and makes this unit extremely vulnerable. The jaws are at all times exposed to hot gases and dust, and this shortens their useful lives. The best materials for casting contact jaws are copper alloys, which offer minimum electrical resistance and high thermal conductivity. Steel jaws also perform satisfactorily in contact with graphitized electrodes.

The pressure at the contact, an increase in which lowers electrical resistance, is of great importance for reducing resistance at the interface between the jaws and electrodes. To improve the service conditions of the contact jaws, it is necessary to increase the contact area and improve the finish on the contact planes.

The contact-jaw hangers bear against the carrier ring. Current is fed to the encased jaws through water-cooled copper tubes. The ring and jaws are encased and also water-cooled.

Current from the furnace transformer is supplied to the furnace through a so-called secondary circuit, which usually consists of three segments. Current is delivered direct from the transformer through a bundle of copper busbars, then through a flexible section ("string") assembled from bundled copper cables, and from the flexible bundles through the water-cooled current-carrying copper tubes to the electrode-holder jaws. Reference [10, page 119] reports a study of various sets of electrical conditions used in smelting out titanium slags. It was established that the best

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smelting results are obtained in operation on the upper voltage stage (133.5 V). It was concluded that this voltage is not the limit. As the voltage is raised, the power supplied is utilized more completely, and this is accompanied by a decrease in power consumption for smelting the slag and an increase in furnace productivity.

#### Flux Smelting

In the smelting of rich titanium slags in electric smelting furnaces, the most important property of the slag is its electrical conductivity. The high melting points of titanium slags (up to and above 1700°C) and their tendency to freeze quickly complicate the smelting process. These complications are aggravated by the high conductivity of the slags. As we noted above, titanium dioxide, a dielectric under mild reducing conditions, acquires electronic conductivity, apparently as a result of the appearance of defects in the rutile lattice owing to partial oxygen loss. The lower titanium oxides and the solid solutions that they form (anosovite and tagirovite) have conductivities 100 times higher than those of silicate slags [10, page 3]. According to [57], a slag containing 15% FeO and 85% TiO<sub>2</sub> has a conductivity of 110 Ω<sup>-1</sup>·cm<sup>-1</sup> at 1700°C, and 130 Ω<sup>-1</sup>·cm<sup>-1</sup> at 5% FeO and 95% TiO<sub>2</sub>.

According to [4, page 24], slags containing up to 40% titanium dioxide have conductivities close to those of silicate slags. At titanium dioxide contents above 50%, the conductivity of the slag rises sharply in both the solid and liquid states. A slag containing 90% TiO<sub>2</sub>, 3.75% SiO<sub>2</sub>, 2.25% FeO, 2% Al<sub>2</sub>O<sub>3</sub>, 2% MgO had a conductivity of 150 Ω<sup>-1</sup>·cm<sup>-1</sup>.

The combination of high conductivity and melting point forces us to seek ways to step up the slag-melting process by adding fluxes. The addition of small amounts of limestone lowers the melting point and conductivity of the slag. Addition of up to 4-5% of calcium oxide gives a sharp decrease in the conductivities of titanium-containing slags.

Study of the TiO<sub>2</sub>-Ti<sub>2</sub>O<sub>3</sub>-CaO system with contents of 4% SiO<sub>2</sub>, 2% Al<sub>2</sub>O<sub>3</sub>, 3% FeO, and 2% MgO indicated that at 5% CaO, the melting

point of a slag with the ratio  $Ti_2O_3:TiO_2 = 1.5:1$  ranges from 1550 to 1600°C [4, page 73].

Increasing the  $Ti_2O_3$  content at any calcium oxide content raises the melting point and viscosity of this system. Nevertheless, addition of calcium oxide reduces these parameters substantially.

TABLE 24  
Melting Point of Slag as a Function of its Composition and  $Ti_2O_3:TiO_2$  Ratio  
(Melting point determined at slag viscosity of 5 P)

| slag no.                                 | contents of components, % |                                |                  |                                |                                |      |      |      |  | slag melting point, °C |
|--|---------------------------|--------------------------------|------------------|--------------------------------|--------------------------------|------|------|------|--|------------------------|
|  | TiO <sub>2</sub>          | Ti <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | FeO  | CaO  | MgO  | Ti <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> |                        |
| slags smelted from arizonite concentrate |                           |                                |                  |                                |                                |      |      |      |  |                        |
| 1  | 43.33                     | 30.91                          | —                | —                              | 0.65                           | 5.08 | —    | 1.56 | 0.62   | 1590                   |
| 2  | 50.30                     | —                              | 3.60             | 3.90                           | 0.77                           | 3.86 | 0.35 | 1.29 | —  | 1555                   |
| 3  | 58.90                     | —                              | 1.9              | 3.55                           | 0.91                           | 3.80 | 0.56 | 1.30 | —  | 1630                   |
| 4  | 65.20                     | —                              | 2.20             | 4.60                           | 1.15                           | 3.66 | 0.62 | 2.63 | —  | 1560                   |
| 5  | 72.78                     | 39.20                          | —                | —                              | —                              | 3.80 | —    | 1.44 | 0.92   | 1618                   |
| 6  | 47.50                     | 33.15                          | —                | —                              | 2.63                           | 4.44 | —    | 1.44 | 0.70   | 1575                   |
| 7  | 52.20                     | —                              | 3.20             | 4.00                           | 2.00                           | 2.10 | 0.70 | 5.20 | —  | 1600                   |
| 8  | 41.27                     | 33.83                          | 2.80             | 3.60                           | 1.66                           | 3.21 | 0.70 | 1.56 | 0.94   | 1580                   |
| 9  | 59.03                     | 21.88                          | —                | —                              | 2.54                           | 3.22 | —    | 1.25 | 0.37   | 1470                   |
| 10                                       | 57.90                     | —                              | 2.40             | 3.45                           | —                              | 2.64 | 1.45 | 2.84 | —  | 1600                   |
| 11                                       | 44.78                     | 33.56                          | —                | —                              | —                              | 3.60 | —    | 1.23 | 0.75   | 1640                   |
| 12                                       | 50.55                     | 27.96                          | —                | —                              | 2.50                           | 4.92 | —    | —    | 0.55   | 1570                   |
| 13                                       | 60.00                     | 22.42                          | —                | —                              | 2.00                           | 4.18 | —    | 1.0  | 0.37   | 1615                   |
| 14                                       | 47.23                     | 34.63                          | —                | —                              | 2.00                           | 4.18 | —    | 1.0  | 0.73   | 1560                   |
| 15                                       | 54.60                     | 28.37                          | —                | —                              | 2.19                           | 3.05 | —    | 1.07 | 0.47   | 1525                   |
| slags smelted from rutilized ilmenite    |                           |                                |                  |                                |                                |      |      |      |  |                        |
| 1  | 60.4                      | 18.5                           | 5.7              | —                              | —                              | 5.3  | —    | 0.30 | —  | 1410                   |
| 2  | 54.6                      | 22.5                           | —                | —                              | —                              | 3.7  | 6.2  | —    | 0.40   | 1410                   |
| 3  | 57.5                      | 25.2                           | —                | —                              | —                              | 2.0  | 4.2  | —    | 0.44   | 1515                   |
| 4  | 58.0                      | 29.0                           | —                | —                              | —                              | 2.7  | 5.2  | —    | 0.50   | 1450                   |
| 5  | 52.5                      | 29.7                           | —                | —                              | —                              | 0.2  | 6.1  | —    | 0.56   | 1517                   |
| 6  | 52.0                      | 35.6                           | —                | —                              | —                              | 2.4  | 2.4  | —    | 0.68   | 1610                   |
| 7  | 51.5                      | 37.2                           | —                | —                              | —                              | 1.4  | 5.3  | —    | 0.72   | 1560                   |

The conductivities of slags to which calcium and magnesium oxides were added were studied in [28, page 95]. In a slag of the composition 3% FeO, 3% SiO<sub>2</sub>, 2% Al<sub>2</sub>O<sub>3</sub>, and 2% MgO, titanium dioxide was replaced by calcium oxide as the latter's content was raised from 0 to 15%. The conductivity of the slag at 1600°C was

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about  $88 \Omega^{-1} \cdot \text{cm}^{-1}$  on addition of 4% CaO and about  $50 \Omega^{-1} \cdot \text{cm}^{-1}$  with 6% CaO.

Addition of magnesium oxide also lowers the conductivity of the slag (addition of 4% MgO lowers slag conductivity at  $1600^\circ\text{C}$  to  $67 \Omega^{-1} \cdot \text{cm}^{-1}$ ).

Addition of limestone as a flux was tested on industrial-furnace melts [16]. The industrial-scale tests confirmed the results of laboratory research. The compositions and melting points of the slags melted out of a rutilized-ilmenite concentrate with a flux are given in Table 24, from which we see that even at a  $\text{Ti}_2\text{O}_3:\text{TiO}_2$  ratio of 0.72, a slag containing 5.3% CaO has a melting point of  $1560^\circ\text{C}$ , while the preceding slag (No. 6), which has a similar  $\text{Ti}_2\text{O}_3:\text{TiO}_2$  ratio and a 2.4% CaO content, melts at a temperature 50 degrees higher.

A mixture of limestone and soda was tested as a flux in [10, page 86]. Addition of 2-3% soda promotes more complete reduction of the titanium, while the addition of limestone lowers the melting point of the slag. On addition of a dolomite flux, the viscosity and melting point of the slag rise [16].

However, our appraisal of these encouraging results obtained with the use of fluxes must be critical when it comes to the production of rich titanium slags for use in the production of titanium tetrachloride. Despite the difficulties that arise in the technology of smelting without fluxes, it is apparently preferable to flux smelting in view of the advantages that are secured in the form of higher titanium contents in the slag-chlorinating process.

#### Smelting without Addition of Fluxes

The features of slag smelting without fluxes include the use of admixtures present in the concentrate as diluents and control of slag melting point by varying its ferrous oxide content. Admixtures of the oxides of aluminum, calcium, magnesium, silicon, and chromium, which are almost always present in appreciable quantities in titanium concentrates, are fluxing components. This applies in particular to the ferrous oxide content in the slag. According to [10, page 3], slags containing more than 10% FeO have

conductivities equivalent to slags containing 4% CaO. According to [58], a slag containing 0.75% CaO, 8.26% FeO, and 85.7% TiO<sub>2</sub> pours satisfactorily from the furnace.

The variation of the FeO and TiO<sub>2</sub> contents in a slag during fluxless smelting is displayed in Fig. 24 [10, page 105], from which we see that the basic peculiarity of the fluxless process is the need to maintain a high ferrous oxide content in the slag through about 70% of the smelting time, after which the slag is refined with addition of a solid reducing agent directly into the melt. In this smelting method, only enough reducing agent to produce a slag with a ferrous oxide content higher than 10% is added to the charge at the outset. But when the entire charge in the furnace has melted, refinement of the slag is initiated by adding reducing agent to it. The reducer is added slowly to prevent the slag from erupting from the furnace.

The conductivity of the melt during refining is of no particular importance in the range in which it can vary, since the electrodes are automatically retracted from the melt and the furnace is operated open-arc during this period in both fluxed and fluxless smelting.

According to [16], a slag containing 18.9% FeO, 21.1% TiO<sub>2</sub>, and 60% Ti<sub>2</sub>O<sub>3</sub> has a conductivity of 75 to 77 Ω<sup>-1</sup>·cm<sup>-1</sup> in the temperature range from 1450 to 1700°C, while a slag containing 5% FeO and 95% TiO<sub>2</sub> has a conductivity that rises from 124 to 134 Ω<sup>-1</sup>·cm<sup>-1</sup> in the same temperature interval. Hence it follows that with increasing conductivity, i.e., as the ferrous oxide of the slag is depleted, the furnace will go into open-arc operation in

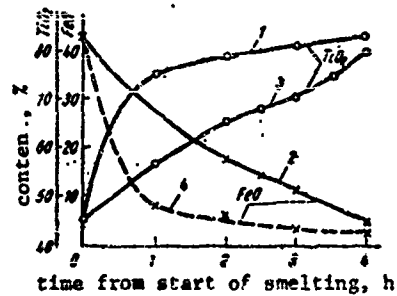


Figure 24. Variation of titanium dioxide and ferrous oxide contents in slag during smelting process. 1 and 2) with reduction from molten slag; 3 and 4) with addition of all reducing agent to the charge.

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The basic difficulty encountered in fluxless smelting is determination of the end of the refining process. A slag containing up to 50% or more of titanium sesquioxide can easily be frozen in the furnace if the ferrous oxide content is lowered below 2-3%. The melting point of the slag then rises sharply, and the furnace power rating is incapable of raising the temperature to keep ahead of ferrous oxide reduction. Titanium lower oxides and oxycarbide accumulate in the slag, and it solidifies quickly. Only a smelter of long experience can detect the onset of slag freezing. A timely injection of unreduced concentrate into the molten slag then returns it to the fluid state.

As we have already noted, ilmenite is characteristically fusible (1380-1400°C) and its ferric oxide content is difficult to reduce. For this reason, the slag-fusing process generally runs ahead of the iron reduction. Even when enough reducing agent was added to the concentrate and carbon briquettes to produce a slag with 3% FeO, a slag containing 14-18% FeO was obtained during the first hour of smelting [16].

This property of ilmenite is utilized in fluxless smelting. The initial charge is compounded with a deficiency of carbon; it melts quickly and then the iron is reduced in the liquid slag until its fluidity limit has been reached. An advantage of this smelting method is that the furnace operates at low temperature on a fusible melt for at least 2/3 of the smelting time. Therefore, as has been shown by specially designed experiments, electric power consumption is practically the same for smelting with and without fluxes [10, page 105].

The utility of fluxless smelting must be examined for each type of titanium concentrate. Generally, all concentrates can be melted without a flux in the intermittent process. Normal slag discharging is ensured by leaving enough ferrous oxide in it to maintain fluidity.

The smelting process consists of a group of operations that must be carried out in sequence. Before charging, it is necessary

to clean the furnace top, removing solidified slag spatter. The charge is distributed uniformly around the furnace. It may be piled higher under individual electrodes only when it is necessary to build up a wall or tap-hole liner. The space between the electrodes and the wall must be filled with charge to preserve the liner. Usually, a mixture of unbriquetted and briquetted charge is smelted. The proportions depend on concentrate composition. For example, 40-50% of powdered charge and 60-50% of briquettes used in smelting rutilized concentrate. The briquetted part of the charge may represent 75-90% for arizonite concentrate.

The charge is briquetted on waffle-iron briquetting presses. Coal pitch or sulfite-cellulose liquor is introduced into the charge as a binder, in amounts ranging from 3 to 6% of charge mass. The briquettes withstand loads from 60 to 250 kg in crushing tests.

The powder charge is loaded into the furnace first and followed by the briquettes. An effort is made to charge the furnace in such a way that the briquettes will not fall against the bottom of the furnace wall. They melt poorly at these points and may collapse at the end of smelting, causing the melt to bubble vigorously and erupt from the furnace.

After charging, the furnace is switched into the first transformer stage (133.5 V). Before switching on, the electrodes are set 200-250 mm above the level of the iron pool to prevent them from shorting across the iron. When the charge has melted around the electrodes and the furnace has built up sufficient power, the automatic system is switched on to regulate the electrical load of the furnace.

In the initial phase, the target of smelting is a slag containing 10 to 20% ferrous oxide. During this phase, the molten slag is saturated with gases liberated as a result of the reduction reactions. At this point the conductivity of the melt is low, so that the work can be done with the electrodes immersed into the slag. After the entire charge has melted, the first smelting phase is over. It takes about 60-70% of the time. Smelting then continues for reduction of the ferrous oxide from the molten slag.

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to clean the furnace top, removing solidified slag spatter. The charge is distributed uniformly around the furnace. It may be piled higher under individual electrodes only when it is necessary to build up a wall or tap-hole liner. The space between the electrodes and the wall must be filled with charge to preserve the liner. Usually, a mixture of unbriquetted and briquetted charge is melted. The proportions depend on concentrate composition. For example, 40-50% of powdered charge and 60-50% of briquettes used in smelting sulfidized concentrate. The briquetted part of the charge may represent 75-90% for arsenic concentrate.

The charge is briquetted on raffle-iron briquetting presses. Coal pitch or sulfite-cellulose liquor is introduced into the charge as a binder, in amounts ranging from 3 to 6% of charge mass. The briquettes withstand loads from 10 to 250 kg in crushing tests.

The powder charge is loaded into the furnace first and followed by the briquettes. An effort is made to charge the furnace in such a way that the briquettes will not fall against the bottom of the furnace wall. They melt poorly at these points and may collapse at the end of smelting, causing the melt to bubble vigorously and erupt from the furnace.

After charging, the furnace is switched into the first transformer stage (157.5 V). Before switching on, the electrolytes are set 40-50 mm above the level of the iron pool to prevent them from shorting across the iron. When the charge has melted around the electrodes and the furnace has built up sufficient power, the automatic system is switched on to regulate the electrical load of the furnace.

In the initial phase, the target of smelting is a slag containing 10 to 20% ferrous oxide. During this phase, the molten slag is saturated with gases liberated as a result of the reduction reactions. At this point the conductivity of the melt is low, so that the work can be done with the electrodes inserted into the slag. After the entire charge has melted, the first smelting phase is over. It takes about 60-70% of the time. Smelting then continues for reduction of the ferrous oxide from the molten slag.

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Toward the end of the first phase, the content of lower titanium oxides in the slag rises and, consequently, so does its conductivity, so that the electrodes are raised and the furnace goes over to open-arc operation.

During the second smelting phase, a reducing agent, usually anthracite, is injected into the melt to continue reduction of the slag. The reducer is added in 40-60-kg batches to avoid severe bumping of the slag and ejection of slag from the furnace. The next batch of anthracite is added after the bubbling of the slag has subsided. At slag ferrous oxide contents below 8%, the anthracite is added in small doses, since the frothing of the slag is especially strong during this period. At this point, the conductivity of the slag is high, and the furnace is in practically continuous open-arc operation.

In addition to quick slag analyses, certain characteristic signs are read to determine the completion of ferrous oxide reduction from the liquid slag: the bath does not stop bumping after addition of one of the reducer batches, or a rabble sample of the slag carries a thin yellow film after quenching in water. The slag is cooled for 20-30 minutes after completion of reduction in order to allow the beads of iron that have remained in the slag to settle. During this time, charge that has adhered to the walls may slide in, in which case the settling time is lengthened by 10-15 minutes. The smelting products are tapped together through the same hole. This is dictated by the fact that titanium slags solidify quickly and plug the tap hole. When iron and slag are released together, the tap hole is heated by the iron, and the slag runs out through it after it has been thoroughly heat and increased in cross section.

The iron and slag are usually discharged into cascaded chill molds. These molds are lined with fireclay brick; the first one under the hole is primed with sand and the subsequent ones, into which the slag flows by gravity, with fine slag. The molds are kept hot at all times so that the priming materials will be thoroughly dry before the smelting products are released.

Before opening, the tap hole is cleaned out with a rabble as far as the hot zone; it is then heated with electric current passed through a steel shunt rod until a drop of iron appears. At this point, the hole is quickly burned open with oxygen. For cold slags, recourse is sometimes taken to further expansion of the discharge hole by continuing the oxygen during discharge.

When boiling slag is released, it may froth and overflow the molds. Frothing is prevented by throwing fine moistened slag into the molds. When routine operations have been established, a quite definite amount of charge that has been established by trial and error is usually smelted out at one time. Nevertheless, occasional overcharging of the furnace may occur and upset the smelting procedure; this is explained by incomplete melting through of the charge in the preceding melt or by incomplete tapping of the slag. Such overcharging of the furnace tends to draw out the reduction and fusion processes, the furnace operates open-arc for longer times, and this is accompanied by cooling of the lower zones of the bath, with intensified bumping of the melt. To arrest this process, a melt of reduced weight is processed, with 1/3 of the usual load in the furnace.

The increase in bath volume that results from washing away of the liner also upsets the smelting routine; reduction and melting of the charge are protracted. The charge that fills the space previously occupied by the liner is last to melt and often produces slides at the end of smelting, which are accompanied by vigorous bumping of the slag. Moreover, softening of the liner is dangerous for the refractory brickwork, with which the molten slag may not come into contact. For this reason, the condition of the liner must be watched at all times.

After a melt has been discharged, the tap hole is usually plugged with a mixture of equal parts of clay and anthracite. After discharge, the pig-iron mold is allowed to stand for 40-60 min, and then the iron is poured into sand molds from under the crust that has formed; this slag crust is then placed in a metal box for dispatch to storage.

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## Production and Smelting of Agglomerate

Smelting of unlumped fine charges in ore furnaces involves increased power consumption and is less productive than smelting of lumped charges. It is practically impossible to smelt finely divided concentrates because of the large amounts of dust that are lost. Agglomeration is one method used to lump concentrate before smelting.

Reference [28, page 50] describes experiments in the agglomeration of a mixture of perovskite and titanomagnetite concentrates in 25:75 proportions. Preliminary laboratory experiments showed that the moisture content in the charge has a strong influence on the quality of the agglomerate and the sintering process. The optimum moisture content was 5-6%. The lumping process becomes very difficult without moistening. The initial concentrate had particle sizes from 0.1 to 0.5 mm.

Industrial-scale experiments were run on sintering machines with a 75-m<sup>2</sup> sintering area. At the perovskite and titanomagnetite concentrate proportions indicated above, 5-5.5% carbon, about 7% moisture, and 25-30% of recycling charge were added to the new charge. Coke fines with an ash content of 15-18% was used as the fuel.

The chemical composition of the resulting agglomerate was as follows (the principal components are listed): 14.19% TiO<sub>2</sub>; 4.6% SiO<sub>2</sub>, 0.6% Al<sub>2</sub>O<sub>3</sub>; 47.04% Fe<sub>2</sub>O<sub>3</sub>; 13.76% FeO; 11.56% CaO; 2.75% MgO; 2.13% Fe. The screen composition of the agglomerate was satisfactory (the yield of minus-five-mm fines was 42.5%).

The agglomerate was melted in a 4500-kVA vaulted ore furnace with self-sintering electrodes. The furnace was lined with magnesite brick and the vault with Dinas brick.

The result was a slag containing an average of 77.3% TiO<sub>2</sub> and 3.27% FeO.

It was established according to [19] that agglomeration of titanium concentrates breaks down the ilmenite (the degree of ilmenite decomposition ranges up to 70%) and forms hematite,

perovskite, anosovite, and other minerals; the reducibility of the agglomerates is improved over that of the ilmenite concentrates.

An agglomerate obtained from an ilmenite concentrate consists of primary mineral granules and newly formed phases. The ilmenite, which is the principal phase in the agglomerates, differs from the original ilmenite. A substantial quantity of newly formed minerals is found in the agglomerate: secondary magnetite, lamellar hematite, and hematite in the form of rims around ilmenite and magnetite grains. As a rule, the hematite is confined to pores. Elongated prismatic black crystals of anosovite are also present in the agglomerate. Dendrites of perovskite, isometric spinel crystals, and crystals of fayalite and baikalite ( $MgTi_2O_4$ ) are encountered. The principal cementing phases in agglomerates obtained under industrial conditions are titanaugite  $m[(CaO \cdot MgO)_2 \cdot SiO_2] \cdot n[CaO(Al, Ti)_2O_3 \cdot SiO_2]$  and a glass. The glass has a composition similar to that of the titanaugite.

Agglomerate obtained from rutilized ilmenite concentrate at  $1300^\circ C$  with a coke content of 4.5% is gray in color with a semi-metallic luster and about 20% porosity; however, its strength is low.

The general relationships that unfold during agglomeration of ilmenite concentrates can be reduced to the following statements: under subjection to high temperatures, the ilmenite decomposes owing to the limited solubility of  $Fe_2O_3$  in  $FeTiO_3$ , with the result that the hematite in the ilmenite is precipitated. The solubility of hematite in ilmenite is quite high at high temperatures. Addition of 2% of slaked lime to the charge results in more active decomposition of the ilmenite with formation of anosovite, perovskite, titanaugite, and iron and glass beads. A lime additive tends to produce a stronger agglomerate.

Thus, the initial processes of slag formation take place during agglomeration.

The work done has demonstrated that agglomeration is quite feasible as a method for preparing a charge of ilmenite concentrate for smelting. However, agglomeration is not used under

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industrial conditions at the present time owing to the relatively small scale of titanium-slag production, which is not enough to justify the installation of the expensive charge-agglomerating machinery.

#### Continuous and Two-Stage Smelting

Organization of a continuous process is an important prerequisite to intensification of titanium-slag smelting. However, there is as yet no industrial method for the production of titanium slag with a low ferrous oxide content in a continuous-flow process.

As we have noted, titanium slags containing less than 8-10% ferrous oxide are very high-melting and can freeze quickly, thus making it difficult to release the pig iron and slag separately from the furnace.

To form a conception of the continuous process, it is necessary to examine the smelting process designed at an electrometallurgical plant constructed in 1950 and belonging to the Canadian firm Quebec Iron and Titanium Corporation (Sorel). This plant has 5 furnaces, each of which smelts about 300 tons of concentrate per day.

The raw material for smelting is an ilmenite ore mined in the Allard Lake region and containing hematite and ilmenite in 2:1 proportions. Table 17 gives the composition of the ore.

The ore is ground to -10 mm and separated by wet screening into two fractions: +14 mesh and -14 mesh. The coarse fraction is concentrated on hydraulic cyclones, while the fine fraction is separated from the slime in a thickener and concentrated in Tempfrey spiral separators. The combined concentrate, which contains 36.8%  $TiO_2$  and 41.8% Fe, is dried and roasted in rotary furnaces fed by exhaust gases from the electric smelting furnaces.

The object of rotary-furnace roasting is evidently to remove sulfur and oxidize part of the iron from the ilmenite in order to improve its reducibility. Thus, the roasting is oxidative.

Anthracite is introduced into the smelting charge as a reducer, in an amount equal to about 16.5% of the concentrate mass.

No flux is added for smelting. The electric furnace is rectangular, with a shaft length of 15.2 m, a width of 6.1 m, and a height of 6.1 m. Furnace power is about 20,000 kVA. The furnaces are of the closed type with suspended vaults, and are lined with magnetite firebrick. A row of 6 graphitized electrodes 620 mm in diameter is installed along the long axis of each furnace. There are two electrodes per phase. The electrodes are traversed automatically by amplidyne-controlled electric motor drives.

The charge is fed continuously through a system consisting of a large number of hoppers and loading chutes, which permits injection of the desired amount of charge into the desired zone of the furnace at the desired rate. The charge is introduced into the furnace in such a way as to prevent contact between the molten slag and the furnace lining, and hence erosion of the latter. The furnaces are run open-arc. Furnace temperature during smelting is about 1650°C. A small positive pressure is maintained in the furnace. A gas containing about 80% CO and 12% H<sub>2</sub> is taken from the furnace and, after washing and compressing, used to heat the rotary furnaces and driers for the anthracite. About 85000 m<sup>3</sup> of gas are obtained from each furnace in a day.

The metal and slag are discharged separately and intermittently from the furnace: the slag 4-6 times a day, and the metal 2-3 times. They are drained down to a certain bath level, which is carefully monitored. The slag is discharged from the furnace directly into chill molds mounted on carts. To speed up cooling, the slag blocks are sprayed with water and dumped onto a platform. It is then broken up into half-inch fragments and sent for storage.

The slag is used basically for pigment production, and has the following composition, in %: 70-72 TiO<sub>2</sub>; 12-15 FeO; 1.5 (max.) Fe<sub>met</sub>; 3.5-5.0 SiO<sub>2</sub>; 4.0 Al<sub>2</sub>O<sub>3</sub>; 1.2 (max.) CaO; 4.5-5.5 MgO; 0.25 (max.) Cr<sub>2</sub>O<sub>3</sub>; 0.5-0.6 V<sub>2</sub>O<sub>5</sub>; 0.2-0.3 MnO; 0.03-0.10 C; 0.025 (max.) P<sub>2</sub>O<sub>5</sub>; 10.0-15.0 Ti<sub>2</sub>O<sub>3</sub> (in TiO<sub>2</sub>).

In addition to the slag produced for pigment titanium dioxide production, the plant makes a slag for use in production of

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metallic titanium; it differs from the former type only in having a somewhat higher content (74-76%) of  $TiO_2$  and less ferrous oxide (8-11%). A major part of the titanium in this slag is bound in  $Ti_2O_3$  (13.0-20.0%).

The iron tapped from the furnace contains 1.6-2.5% C, up to 0.11% S, and 0.025% P. The sulfur is first removed from it in the ladles and then in electric furnaces, at which point the so-called Sorel metal is ready for delivery.

Thus, continuity of the titanium slag's melting process at Sorel is provided by leaving a high ferrous oxide content in the slag to render it readily fusible and make it possible to discharge the smelting products separately from the furnace. The substantial contents of  $SiO_2$ ,  $Al_2O_3$ , and  $MgO$  in the charge and slag, which act as fluxing components, also promote continuity of smelting.

The process at the Sorel plant is economical because of the high yield of pig per ton of slag (0.74 ton); as a result, it is advantageous to refine the iron and sell it as a commercial product in view of the large production scale.

The experience gained at this plant is unquestionably of interest for the organization of continuous titanium slag smelting in the USSR.

In the Soviet Union, the A.A. Baykov Institute proposed a technology for continuous smelting of ilmenite concentrate by the so-called two-stage method in 1962 [10, page 96]. The essential point of this technology consists in preliminary reduction of the iron oxides from the ilmenite concentrate in the solid stage. In the proposed process, the ilmenite concentrate is briquetted in a mixture with carbon and reduced in a shaft or tunnel furnace at  $1300^\circ C$  to produce a cake. These cakes are smelted without the formation of boiling slags, and the  $Ti_2O_3:TiO_2$  ratio ranges from 0.15 to 0.20. This slag melts at about  $1500^\circ C$ . Although the process has not yet advanced beyond the laboratory testing stage, it is unquestionably of interest.

The two-stage smelting method is characterized by reduction of the iron oxides present in the concentrate to the metal in the solid phase during a first stage. A wide variety of methods may be used for the first-stage concentrate reduction, just as in the direct reduction of iron ores.

In the second stage, the concentrate reduced in the first stage is smelted in an ore furnace; no substantial amount of lower titanium oxides accumulates in the slag during this process. Experiments in the smelting of prereduced concentrate were carried out in a scaled-up laboratory furnace [10, page 96]. They showed that smelting proceeds quietly, without bubbling of the melt and with substantially lower electric power consumption. It is suggested that the prereduced concentrate might be smelted without adding additional reducing agent [10, page 3]. The preliminary reduction should be performed on granules formed in pan granulators or on briquettes mixed with reducing agent.

It has been established under industrial conditions that briquetting of titanium concentrates mixed with a reducer makes it possible to step up the iron-oxide reduction process during smelting [10, pages 16, 105]. However, when briquettes that have not been prereduced are used, two undesirable effects result [59]:

1) the briquetted charge undergoes sintering, and the gas-impermeable layer that formed in this process prevents contact with the reducer and retards smelting. For this reason, briquette smelting is often combined under industrial conditions with periodic loading of an unbriquetted powder charge into the furnace;

2) during smelting of briquettes, the reduction of iron oxides takes place at high temperatures and is accompanied by reduction of titanium dioxide to a lower oxidation state, thus raising the melting point of the slag and causing practically useless expenditure of power on this process, since the lower titanium oxides oxidize in air on cooling of the slag, forming titanium dioxide.

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Compositions and Properties of Titanium Slags

Table 25 gives typical compositions of slags smelted out of the three types of titanium concentrates that we have discussed. These data pertain to fluxless smelting. The titanium dioxide contents are indicated here as the results of conversion of all of the titanium present in the slag to titanium dioxide. During storage, the slag crumbles (decrepitates) as a result of recrystallization accompanying oxidation of the lower titanium oxides to the dioxide. The mass of the slag increases, and its titanium dioxide content declines by 3-6%.

TABLE 25  
 Typical Compositions of Titanium Slags Smelted Out of  
 Various Types of Raw Material without Addition of Fluxes  
 [10, pages 16, 58, 105]

| component                      | concentrate, % |           |          |
|--------------------------------|----------------|-----------|----------|
|                                | arizonite      | rutilized | ilmenite |
| TiO <sub>2</sub>               | 87.8           | 85.7      | 89.0     |
| FeO                            | 3.18           | 6.5       | 2.7      |
| SiO <sub>2</sub>               | 2.79           | 5.68      | 5.2      |
| CaO                            | 0.29           | 0.72      | 1.2      |
| Al <sub>2</sub> O <sub>3</sub> | 5.11           | 1.9       | 6.1      |
| MgO                            | 2.16           | 2.0       | 5.6      |
| MnO                            | 1.68           | ~1.0      | 1.84     |
| Cr <sub>2</sub> O <sub>3</sub> | 1.08           | —         | —        |
| V <sub>2</sub> O <sub>5</sub>  | 0.15           | 0.14      | —        |
| S                              | 0.008          | —         | —        |
| C                              | 0.3            | —         | —        |
| TiO <sub>2</sub> + CaO + MgO   | 5.24           | 9.87      | 12.0     |

The ferrous oxide content in the slags indicates that it is possible to produce a slag with a rather low content of this oxide in fluxless smelting. Slag smelted from rutilized ilmenite concentrate, where the ferrous oxide content is twice that in a slag smelted out of arizonite concentrate, is an exception. This is because of the comparatively low impurity content in the rutilized concentrate, a consequence of which is that more ferrous oxide is left in slags smelted from this concentrate to ensure fluidity. However, it is necessary to state a reservation: the lower limit of ferrous oxide content in the slag also depends on the proficiency of the smelting process. Slags containing less than 2-3% of

ferrous oxide are rarely produced because of the sharp deterioration of their fluidity that results from the increased contents of lower titanium oxides.

The most stable crystalline form of high-titanium slags produced under industrial conditions is anosovite, whose temperature of formation varies as a function of the content of isomorphous impurities and titanium ions in various valence states that are dissolved in it.

Anosovite incorporates titanium ions of all valences, and di- and trivalent titanium ions may substitute metal ions in the anosovite that have similar ionic radii (for example,  $Mg^{2+}$ ,  $Fe^{3+}$ , etc.). Calcium ions, whose radii are considerably larger than that of titanium (1.01 Å), cannot substitute titanium ions, and calcium is therefore not a constituent of anosovite; the same applies to silicon. Calcium and silicon are the base for formation of a new compound — titanogite or silicate slag cement glass:  $m[(CaO \cdot MgO)_2 \cdot SiO_2] \cdot n[CaO(Al, Ti)_2O_3 \cdot SiO_2]$ . The temperature at which titanogite forms is about 1300°C. According to [24], anosovite has a density of 4.4 and titanogite a density of 3.8 g/cm<sup>3</sup>.

Anosovite has a higher melting point than the other slag components and is first to crystallize from the slags. On subsequent cooling, the anosovite crystals are cemented by titanogite.

While anosovite forms on the basis of the  $Ti_3O_5$  lattice, a new mineral based on the rhombohedral lattice of  $Ti_2O_3$  forms during the next reduction stage (when the slag contains more than 70% titanium dioxide); this is tagirovite, whose formula is [42]



which is a solid solution intermediate between compounds of the types  $MeO \cdot TiO_2$  and  $Me_2O_3$ . In tagirovite, titanium has all of its three valence states, and the tagirovite lattice may incorporate impurities of di- and trivalent metals with ionic radii close to that of titanium.

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Solid solutions of the  $Ti(C, O)$  type form on reduction of tagirovite. However, the principal phase in real slags is anosovite, and only at high titanium dioxide contents is tagirovite detected in them. Two varieties of anosovite — a pink variety (the predominant,  $Ti_2O_3$ -rich form) and a bluish-gray variety with a smaller titanium sesquioxide content — were found in a titanium-rich slag of the composition [60]: 90.1%  $TiO_2$ ; 2.7%  $Fe_{tot}$ ; 0.81%  $Fe_{met}$ ; 3%  $Al_2O_3$ ; 2.35%  $SiO_2$ ; 0.67%  $CaO$ ; 2.6%  $MgO$ ; 1.45%  $Cr_2O_3$ ; 1.1%  $MnO$ ; 3.6%  $TiO$ ; 28.4%  $Ti_2O_3$ ; tagirovite was not detected [80]. It appears that precipitation of the tagirovite phase and  $Ti(C, O)$  intervenes at an even higher titanium dioxide content in slags with low calcium oxide contents [47, 53, 79].

Perovskite ( $CaO \cdot TiO_2$ ) is formed in slags in which up to 3-5%  $CaO$  is present.

The presence of  $SiO_2$  in the slag results in the formation of a low-melting eutectic (see Figs. 19-21) that does not participate in the reduction processes.

An ilmenite phase is detected in slags containing more than 8-10%  $FeO$  [24, page 50]. As the  $MgO$  content is raised (10-14%), solid solutions based on magnesium orthotitanate ( $Mg, Fe$ ) $_2TiO_4$ , geikielite ( $MgTiO_3$ ), baikovite ( $MgO \cdot Ti_2O_3$ ), and forsterite ( $Mg_2SiO_4$ ) are also detected.

The presence of magnesium oxide in the slags in the form of the dititanate  $MgO \cdot 2TiO_2$  helps convert the oxide  $Ti_3O_5$  to anosovite [10, page 42]. The reaction of  $Ti_3O_5$  with magnesium oxide was studied in [28, page 80]. It was established that  $MgO \cdot TiO_2 \cdot Ti_2O_3$  solid solutions were formed in the slag on addition of  $MgO$  in the amount of 3.85% of the  $Ti_3O_5$  mass. The hypothesis was advanced that  $MgO$  and  $Ti_3O_5$  react as follows:



The resulting stable compound — geikielite and titanium sesquioxide — forms a solid solution. The magnesium oxide probably dissolves in the anosovite lattice in the form of the dititanate  $MgO \cdot 2TiO_2$ , which is detected in the form of a monomineral phase, magnesium anosovite  $MgTi_2O_5$ . Specially designed

experiments confirmed that the addition of 1.95% geikielite to  $Ti_2O_3$  results in its complete solution in the sesquioxide with solid solution formation.

Like calcium oxide, magnesium oxide binds titanium dioxide, inhibiting its reduction to a lower oxidation stage. As an isomorphous admixture to minerals based on titanium sesquioxide, magnesium oxide raises the melting point of the titanium slag, with the detrimental consequences for the smelting process.

Fewer experimental data are available on the influence of  $Al_2O_3$  on the properties of titanium slags. We may conclude from [28, pages 42, 80] that, like  $MgO$ , an  $Al_2O_3$  admixture promotes the formation of anosovite. However, in slags containing  $TiO_2$ , more than 75% of the  $Al_2O_3$  dissolves in the tagirovite, forming a phase that can be represented schematically by the formula  $m(Fe, Mg, Mn)O \cdot TiO_2 \cdot n(Ti, Al, Fe)_2O_3$ .

Inspection of the phase diagram of the  $Al_2O_3$ - $TiO_2$  system indicates that the presence of small amounts of aluminum oxide in the slag has no appreciable effect on its fusability. Thus, a slag containing 3%  $FeO$ , 3%  $Al_2O_3$ ; 2%  $Cr_2O_3$ ; 2%  $SiO_2$ ; and 3%  $MgO$  has a melting point of  $\sim 1600^\circ C$  even at a  $Ti_2O_3$ : $TiO_2$  ratio of 1.25. As the  $Ti_2O_3$ : $TiO_2$  ratio is lowered to 0.75, the slag melting point drops to  $1550^\circ C$  (Fig. 25). The slag has about the same melting point when the  $FeO$  content is raised to 10% and that of  $Al_2O_3$  to 10%.

A higher  $Al_2O_3$  content in the slag results in the formation of spinel ( $MgO \cdot Al_2O_3$ ) and titanogite [15].

Like ferrous oxide, magnanous oxide tends to lower the fusability of the slag. Even in the insignificant quantities in which they are present in rich titanium slags, chromium oxides also tend to lower slag melting points. This is illustrated by Fig. 25 [16] as it applies to  $Cr_2O_3$ . Slag fusability is considerably lower at a  $Cr_2O_3$  content of about 3%. Reduction of chromic oxide from the slag begins at a slag content of less than 10% ferrous oxide, and the more completely the ferrous oxide is reduced, the greater is the decline in slag chromium content.



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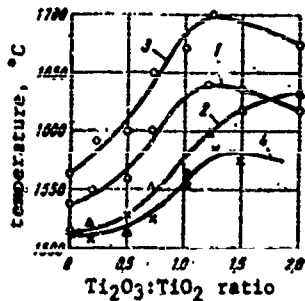


Figure 25. Melting points of titanium slags as functions of  $Ti_2O_3:TiO_2$  ratio and contents of  $FeO$ ,  $SiO_2$ ,  $MgO$ ,  $Cr_2O_3$ , and  $Al_2O_3$ :

1 - 3%  $FeO$ ; 10%  $Al_2O_3$ ; 2%  $Cr_2O_3$   
 2%  $SiO_2$ ; 2%  $MgO$ ; 2 - 3%  $FeO$ ; 3%  
 $Al_2O_3$ ; 2%  $Cr_2O_3$ ; 2%  $SiO_2$ ; 2%  $MgO$ ;  
 2 - 3%  $FeO$ ; 10%  $Al_2O_3$ ; 2%  $SiO_2$ ; 2%  
 $MgO$ ; 2 - 10%  $FeO$ ; 10%  $Al_2O_3$ ; 2%  
 $Cr_2O_3$ ; 2%  $SiO_2$ ; 2%  $MgO$

established that up to 10-15% of  $Ti_2O_3$  depresses the melting point and viscosity of the slag and then increases it [sic] at higher contents. Thus, in order to obtain slags with low viscosity at 1500-1600°C, it is necessary to prevent the accumulation of lower titanium oxides in them. Extremely rapid smelting is the most important prerequisite for this.

The viscosity and fusability of the slags are strongly influenced by their contents of ferrous oxide and chromic oxide. An increase in the sum of these components makes it possible to lower slag viscosity even when the content of lower titanium oxides is quite high.

Electrical conductivity is another important technological property of titanium slags. Certain data characterizing the variation of slag conductivity were given earlier in the description of flux smelting. It should be noted that little study has been devoted to the conductivities of titanium slags.

A typical property of rich titanium slags is their tendency to crumble spontaneously on cooling in air. Screen analysis of the crumbled slag indicates that it contains 86.16% of the fraction  $-1.6+0.175$  mm, and that the remainder is finer [60]. A study of this friability of the slags has shown that it apparently results from oxidation of the lower titanium oxides present in the slag [16]. However, the mineralogical composition of spontaneously crumbled slag has not yet been definitely established.

Pig Iron Produced from Smelting of Titanium Slags

Table 26 lists data on the composition of pig irons smelted out of the above three types of concentrates. On the basis of carbon content, the pig may be classified as chilled. A regular

TABLE 26  
Impurity Contents in Pig Iron Smelted Out of Various Concentrates [10, pages 16, 58, 105]

| concentrate              | impurities, % |      |      |       |       |              |      |      |      | pig iron yield, % of total pigslag |
|--------------------------|---------------|------|------|-------|-------|--------------|------|------|------|------------------------------------|
|                          | C             | Mn   | Mo   | Cr    | Ti    | V            | P    | S    | H    |                                    |
| arizonite . . .          | 2.2           | 0.37 | 0.1  | 1.1   | 0.023 | not detected | 0.16 | —    | —    | 20-21                              |
| rutilized ilmenite . . . | 1.80          | 0.88 | 0.08 | 0.026 | 0.13  | —            | —    | 0.21 | —    | 27-30                              |
| ilmenite . . .           | 2.52          | 0.27 | 0.14 | 0.13  | 0.08  | 0.10         | 0.10 | 0.23 | 0.08 | 42                                 |

decrease in carbon content with decreasing iron yield is characteristic for the compositions given in Table 26. The highest iron yield is obtained from smelting of ilmenite concentrate, which contains more iron.

According to [16], 96.5% Fe; 11.8% Si; 45.8% V, and 0.85% Ti go over into the iron during ilmenite concentrate smelting. When arizonite concentrate is smelted, on the other hand, only 87.5% of the Fe, about 18-20% of the Cr, about 3.5% of the Si, and 0.3% of the V are extracted into the iron.

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The extraction percentages of these components into the iron are governed by the initial concentrate composition and the mass ratio of the iron and slag.

Iron containing more titanium, silicon, and chromium can be produced in small furnaces. Thus, the iron from experimental smeltings in a closed 250-kVA furnace contained 1.92% C, 1.95% Ti, and 1.05% Si.

The greatest practical interest attaches to extraction of chromium into the iron from arizonite concentrate, in which its content sometimes ranges up to 5% (see Table 26). Specially designed studies [29, page 22] brought out the relationships that determine extraction of chromium into the iron. It was established that the transfer of chromium to the iron depends to a major degree on the iron's carbon content. When about 3% C is present in the iron, its chromium content rises to 2.5%.

The extraction of chromium into the pig is also influenced by the yield of iron on the slag and the slag ferrous oxide content. On addition of metal to the slag, a slag containing 0.1-0.2% Cr can be obtained. For better extraction of the chromium into the iron, the ferrous oxide content in the slag must be below 3%. In view of the difficulty of extracting chromium into the iron, it is more advantageous to extract the chromium during concentration. Reference [29, page 22] demonstrates the practical feasibility of partial magnetic separation of the chromium from the concentrate.

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PART III  
PRODUCTION AND PURIFICATION OF  
TITANIUM TETRACHLORIDE

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## Chapter 9

### CHLORINATION OF TITANIUM-CONTAINING MATERIALS

Titanium tetrachloride is prepared either by direct chlorination of titanium-containing concentrates and slags or by chlorination of pure titanium oxide obtained by hydrometallurgical refinement of these materials. At the present time, the former method is most economical and is the one most widely used in world industrial practice.

The advantages of the chlorination method:

1. The high reactivity of gaseous chlorine at elevated temperatures and its relatively low cost, which still shows a downward trend as a result of the development of electrolytic methods of producing metals and chlorine from chlorides, e.g., the electrolysis of magnesium and sodium chlorides.
2. The relative simplicity and efficiency of separating the titanium tetrachloride formed during chlorination from the other chlorides that accompany it in this process.
3. The high productivity of the basic technological equipment in the chlorination and chloride-separation processes.

The chlorination method makes it possible to break up the titanium-containing materials quite completely and quickly and separate the basic mass of the impurities from the titanium tetrachloride during the chlorination process itself and on

condensation of the resulting products.

#### Molecular Structure and Properties of Titanium Tetrachloride

At room temperature, pure titanium tetrachloride is a colorless mobile liquid. The technical product has colors varying from yellowish-green to dark red, depending on the amount and type of the impurities present in it. The titanium tetrachloride molecule has the form of a regular tetrahedron with the titanium nucleus at its center and the nuclei of the chlorine atoms at its vertices. The distance between chlorine nuclei in the molecule is  $3.61 \pm 0.04 \text{ \AA}$ , and that between the titanium and chlorine nuclei is  $2.10 \pm 0.04 \text{ \AA}$  [1]. Because of these structural features, the  $\text{TiCl}_4$  molecule has no dipole moment, and there is a weak intermolecular interaction in liquid and solid titanium tetrachloride. As a result, the latter is characterized by relatively low melting point ( $-25^\circ\text{C}$ ), boiling point ( $136.5^\circ\text{C}$  at  $P = 760 \text{ mm Hg}$ ), and heat of vaporization ( $45 \text{ cal/g}$  at  $136^\circ\text{C}$ ). Density determinations made on vaporized titanium tetrachloride at  $96^\circ\text{C}$  and  $191 \text{ mm Hg}$  indicate that it consists of single molecules [2]. According to calculation, the critical temperature is about  $628^\circ\text{K}$  [3]. The density of liquid titanium tetrachloride at  $19.84^\circ\text{C}$  is  $1.72796 \text{ g/cm}^3$ , and that of the solid form at  $-79^\circ\text{C}$  is  $2.06 \text{ g/cm}^3$ .

The heat of formation of liquid titanium tetrachloride from the elements at  $20^\circ\text{C}$  is  $185 \text{ kcal/mole}$ , and the entropy of formation is  $47.9 \text{ cal/(mole}\cdot\text{deg)}$ . The heat capacities of titanium tetrachloride: solid ( $-25^\circ\text{C}$ )  $31.0 \text{ cal/mole}$ , liquid ( $+21^\circ\text{C}$ )  $36.6 \text{ cal/mole}$ , vapor ( $20$ - $136^\circ\text{C}$ )  $24.5 \text{ cal/mole}$ . Pure titanium tetrachloride has practically zero electrical conductivity [4]. The viscosity of titanium tetrachloride is  $0.00826 \text{ P}$ , at  $20^\circ\text{C}$  and  $0.01012 \text{ P}$  at  $0^\circ\text{C}$ .

Titanium tetrachloride is a chemically active compound that reacts with many substances at room temperature or on heating.

At room temperature, titanium tetrachloride does not react with thoroughly dried air. If, however, the air contains moisture, a white smoke forms immediately as a result of formation of solid hydrolysis products. Dry oxygen reacts with titanium

tetrachloride:  
chlorine:

The reaction with hydrogen on contact with titanium is complete. The equation is:

Liquid titanium tetrachloride is a powerful explosive solvent, and it dissolves many substances. On contact with titanium, incomplete hydrolysis products are formed, such as  $\text{TiOCl}_2$ , titanium tetrachloride, and hydrogen chloride.

Hexachloroantimonate of titanium tetrachloride is a black product [6]. The reaction of titanium tetrachloride with hydrogen is described in [9].

Iron tetrachloride is a black product [6].

At room temperature, titanium tetrachloride reacts with hydrogen to form titanium trichloride and hydrogen chloride.

tetrachloride above 500°C with formation of titanium dioxide and chlorine:



The rate of this reaction rises rapidly with temperature. In contact with water, titanium tetrachloride is subject to almost complete hydrolysis in accordance with the following overall equation:



Liquid titanium tetrachloride reacts especially violently, almost explosively, with water. Some of the  $\text{TiO}_2(\text{aq})$  that is formed dissolves, and some of it is precipitated in the form of a gel. When titanium tetrachloride is treated with a small amount of water, incomplete-hydrolysis products with indeterminate compositions are formed, depending on conditions [7]. Most stable among these is  $\text{TiOCl}_2$  [8]. At temperatures above 400°C, water vapor and titanium tetrachloride react with formation of the dioxide and hydrogen chloride.

Hexachlorotitanic acid  $\text{H}_2\text{TiCl}_6$  forms in concentrated hydrochloric acid solution on passage of hydrogen chloride through it [6]. The potassium salt of this acid can be prepared in the solid state [9]. Metals and hydrogen have a characteristic reducing action on titanium tetrachloride. Depending on conditions and the reducing agent used, the trichloride, dichloride, and even elementary titanium may be formed. Metallic copper reacts with titanium tetrachloride at room temperature, with formation of a black product on the copper surface. According to Koontz and Nicholson [5], the process involves the reactions



Iron does not act on titanium tetrachloride at red incandescence [6].

At the boiling point, titanium tetrachloride reacts with hydrogen sulfide to form titanium sulfochloride and sulfide:





When titanium tetrachloride vapor is passed over hot metal sulfides, titanium disulfide and the chloride of the corresponding metal are formed:



Titanium tetrachloride forms when  $\text{TiCl}_4$  is reacted with titanium disulfide [6]:



Titanium tetrachloride reacts with hydrocarbons, esters, alcohols, aldehydes, ketones, cyanides, acids, acid derivatives, amines and nitriles, and azo compounds. Carbon tetrachloride and, to all appearances, other chlorinated hydrocarbons are inert with respect to titanium tetrachloride.

#### Thermodynamic Background of Chlorination

The chlorination process is carried out at 700-1000°C under industrial conditions. Since the reactions that take place during chlorination arrive at equilibrium comparatively quickly at these temperatures, many aspects of the process can be explained by reference to thermodynamic relationships.

The titanium concentrates subject to chlorination are complex oxide systems.

However, to ascertain qualitative relationships in first approximation, they can be regarded as mechanical oxide mixtures.

Titanium dioxide reacts with chlorine in accordance with the equation



The change in the standard isobaric potential of this reaction at 1000°K is  $\Delta Z_{1000}^\circ = 30.4$  kcal, and the heat effect  $-\Delta H_{1000} = -45.8$  kcal. Consequently, the equilibrium constant of Reaction (9) equals

$$K_{1000}^\circ = 2.24 \cdot 10^{-7} = \frac{P_{\text{TiCl}_4} \cdot P_{\text{O}_2}}{P_{\text{Cl}_2}^2}$$

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According to this reaction,  $P_{TiCl_4} = P_{O_2}$ . Since the total gas pressure in the system is one atmosphere, the chlorine partial pressure equals  $P_{Cl_2} = 1 - (P_{TiCl_4} + P_{O_2}) = 1 - 2P_{TiCl_4}$ . Using these relationships, we find that at 1000°K, the equilibrium partial pressure of the titanium tetrachloride vapor for the chlorination reaction of titanium dioxide is  $4.78 \cdot 10^{-4}$  atm. This corresponds to a tetrachloride vapor concentration of ~0.05% (by volume) in the vapor-gas mixture. At 1000°K,  $\frac{\partial \ln K}{\partial T} = \frac{\Delta H}{RT^2} \approx 2.3 \cdot 10^{-2} > 0$ .

(7)

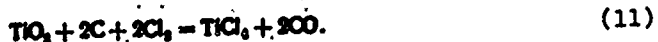
With rising temperature, therefore, the equilibrium constant of Reaction (9) increases. The equilibrium titanium tetrachloride concentration in the gaseous chlorination products increases accordingly, reaching ~0.5% (by volume) at 1000°C, when the equilibrium chlorine concentration is ~99% (volumetric).

(8)

The thermodynamic data given above indicate that it is practically impossible to design an effective process for acquisition of titanium tetrachloride from the dioxide at temperatures below 1000°C on the basis of Reaction (9), since the degree of utilization of the chlorine and chlorinator productivity would be extremely low. To shift the chlorination-reaction equilibrium to the right, it is necessary to bind the oxygen liberated as the oxides are chlorinated. For this purpose, a carbon reducer is added to the charge. In this case, the chlorination reaction proceeds according to the following over-all equations:

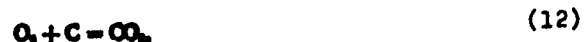


and



Since the change in isobaric potential as a result of the reaction does not depend on the reaction mechanism, each of these equations can be regarded from the thermodynamic point of view as the sum of Reaction (9) and one of the carbon-combustion reactions

(9)



Thus,  $\Delta Z_{10}^\circ = \Delta Z_9^\circ + \Delta Z_{12}^\circ$  and  $\Delta Z_{11}^\circ = \Delta Z_9^\circ + \Delta Z_{12a}^\circ$ . At 1000°K,  $\Delta Z_{10}^\circ$  and  $\Delta Z_{11}^\circ$  equal -64.0 kcal and -64.9 kcal, respectively, and the equilibrium constants of these reactions are:

$$K_{10,1000} = \frac{P_{TiCl_4} \cdot P_{CO_2}}{P_{Cl_2}} = 10^{14} \quad (13)$$

$$K_{11,1000} = \frac{P_{TiCl_4} \cdot P_{CO}^2}{P_{Cl_2}} = 10^{14.2} \quad (14)$$

Both reactions proceed almost completely to the right in practice. Unlike Reaction (9), therefore, the chlorination of titanium dioxide in the presence of carbon can give a high degree of chlorine utilization and high process productivity, assuming selection of conditions under which the reaction proceeds rapidly enough.

Reactions (10) and (11) take place simultaneously during the chlorination of titanium dioxide. Consequently, calculation of the equilibrium composition of the gaseous products in the chlorinator requires simultaneous solution of a system of equations expressing the equilibrium conditions of Reactions (10) and (11), the mass-balance conditions in the system, and equality of the total pressure to one atmosphere:

$$\frac{P_{TiCl_4} \cdot P_{CO_2}}{P_{Cl_2}} = K_{10} \quad (15)$$

$$\frac{P_{TiCl_4} \cdot P_{CO}^2}{P_{Cl_2}} = K_{11} \quad (16)$$

$$P_{TiCl_4} + P_{Cl_2} + P_{CO} + P_{CO_2} = 1, \quad (17)$$

$$P_{TiCl_4} = P_{CO_2} + \frac{P_{CO}^2}{2} \quad (18)$$

The ratio

$$K_{20} = \frac{K_{11}}{K_{10}} = \frac{P_{CO}}{P_{CO_2}} \quad (19)$$

represents the equilibrium constant of the Boudouard reaction:



If  $K_{20} \gg 1$  (temperature  $\geq 1000^\circ C$ ), then  $p_{CO_2} \ll p_{CO}$ . In this case, the equilibrium of Reaction (10) can be excluded from consideration in computing the equilibrium gas composition, and we can assume that the chlorination reaction proceeds by Eq. (11) alone.

If  $K_{20} \ll 1$  (temperature  $\leq 400^\circ C$ ), then  $p_{CO_2} \gg p_{CO}$ . In this case, Reaction (11) need not be taken into consideration in

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computing the equilibrium gas-phase composition. In the intermediate temperature range, it is necessary to consider the equilibria of both reactions. At 700-800°C, the equilibrium constants of Reactions (10) and (11) differ relatively little from one another despite the substantial difference between the heat effects. Thus,

$$-\Delta H_{10,1000^\circ K} = 48.4 \text{ k/cal};$$

$$-\Delta H_{11,1000^\circ K} = 7.6 \text{ k/cal}.$$

Thus, the amount of heat liberated as a result of Reaction (10) for the 2 moles of chlorine is 40.8 kcal larger than the heat effect of Reaction (11). The same difference is also observed between the heat effects in chlorination of other oxides. This must be taken into account in figuring chlorinator heat balance.

In selecting the reducing reagent, it is necessary to consider the equilibria of all of the independent reactions that may occur in the system under the particular conditions. As an example, let us consider the chlorination reaction with participation of a certain reducing agent whose molecule we shall denote by the symbol E. The following side processes (22, 22a, 22b) will probably take place together with the main Reaction (21) in the system under consideration:

(15)

(16)

(17)

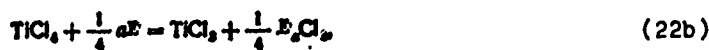
(18)



(19)



(20)



where  $a$  is a positive whole or fractional number  $\leq 4$ .

The reactions in which titanium compounds are reduced (22a and 22b) can take place under equilibrium conditions only in the practically total absence of chlorine in the gases, since the equilibrium constants of these reactions are very small by comparison with those of Reactions (21) and (22), respectively, regardless of the nature of the reducing agent. Progress of the

side reaction (22) is undesirable owing to the unproductive consumption of chlorine for formation of  $E_aCl_4$ .

Carbon, which is usually used as a reducer in chlorine chlorination of titanium dioxide, is attractive not only for its availability, but also because practically no side reactions take place when it is used.

In the presence of side reactions, the number and composition of the phases existing at equilibrium will vary, depending on the component proportions in the starting mixture, the chlorination conditions, and the nature of the reducer. We shall limit ourselves to examination of a single particular case. Let us assume that the process takes place at atmospheric pressure and a constant temperature in the system (the chlorinator). Let us assume further that the starting substances are  $TiO_2$ , E, and  $Cl_2$ , and that the  $TiO_2$ , E,  $E_aO_2$ , and  $E_aCl_4$  form separate condensed phases. Assuming that equilibrium is established instantaneously in the system, let us find how the chlorine is distributed between  $TiCl_4$  and  $E_aCl_4$  at the end of chlorination. Only the oxidized forms —  $TiO_2$ ,  $E_aO_2$ ,  $TiCl_4$ , and  $E_aCl_4$  — can be stable compounds under these conditions. Thus Reactions (22a) and (22b) need not be considered in the thermodynamic analysis.

In accordance with the conditions adopted, the equilibrium constants of Reactions (21) and (22) will be expressed as follows:

$$K_{21} = \frac{P_{TiCl_4}}{P_{Cl_2}^2}, \quad (23)$$

$$K_{22} = \frac{1}{K_{21}}. \quad (24)$$

The chlorine partial pressures calculated with Eqs. (23) and (24) using  $P_{Cl_2} + P_{TiCl_4} = 1$  are

$$P_{Cl_2} = \frac{-1 + \sqrt{1 + 4K_{21}}}{2K_{21}}, \quad (25)$$

$$P_{Cl_2} = \left(\frac{1}{K_{21}}\right)^{1/2} \quad (26)$$

(we disregard the vapor pressures of the condensed phases). At equilibrium, the system may be under the partial pressure of

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chlorine alone. However, as we see from (25) and (26), this condition cannot be satisfied at an arbitrarily assigned temperature for Reactions (21) and (22). Simultaneous occurrence of these reactions is therefore impossible. The one for which the equilibrium chlorine partial pressure is lower will take place first in the system. It follows from (25) and (26), for example, that if  $K_{21} > K_{22}$ , Reaction (21) will take place. With  $(K_{21})^{1/2} \gg 1$ , the condition for occurrence of (22) takes the form  $K_{22} > K_{21}$ . The last two conditions are equivalent to

$$\Delta Z_{21}^0 - \Delta Z_{22}^0 < 0, \quad (27)$$

$$\Delta Z_{21}^0 - \Delta Z_{22}^0 > 0. \quad (28)$$

The exchange-reaction equation is



and represents the difference between the equations of Reactions (21) and (22). The change in standard isobaric potential for this reaction is given by the difference

$$\Delta Z_{21}^0 - \Delta Z_{22}^0 - \Delta Z_{23}^0 \quad (30)$$

whose sign, according to Conditions (27) and (28), determines the sequence in which Reactions (21) and (22) occur.

Thus, if  $\Delta Z_{21}^0 < 0$  and the  $\text{TiO}_2:E$  ratio in the initial mixture is not below stoichiometric according to Eq. (21), all of the chlorine will be bound in  $\text{TiCl}_4$  at the end of the process. If the initial mixture contains an excess of E, it will react with the chlorine after Reaction (21) has been completed. If  $\Delta Z_{21}^0 > 0$  and  $(K_{21})^{1/2} \gg 1$ , Reaction (21) will be practically absent, and all the chlorine will be bound into  $E_2\text{Cl}_4$ .

In Reaction (21), in which we are interested, the maximum chlorine utilization will be

$$\epsilon = \frac{n_{\text{Cl}_2} - n_{\text{Cl}_2}'}{n_{\text{Cl}_2}} = \left[ 1 - \frac{n_{\text{Cl}_2}'}{n_{\text{Cl}_2}} \right], \quad (31)$$

where  $\epsilon$  is the maximum degree of chlorine utilization,  $n_{\text{OCl}_2}$  is the number of gram-molecules of chlorine entering the chlorinator during a certain time interval, and  $n_{\text{pCl}_2}$  is the number of gram-

molecules of chlorine leaving the chlorinator during the same time with the equilibrium vapor-gas mixture.

Since the total pressure is 1 atmosphere, the chlorine partial pressure is numerically equal to its molar fraction:

$$P_{Cl_2} = \frac{n_{Cl_2}}{n_{Cl_2} + n_{TiCl_4}}; n_{TiCl_4} = \frac{n_{Cl_2} - n_{Cl_2}}{2} \quad (32)$$

where  $n_{TiCl_4}$  is the number of gram-molecules of  $TiCl_4$  leaving the chlorinator with the equilibrium vapor-gas mixture.

Substituting these expressions into the formula for  $\epsilon$ , we finally obtain

$$\epsilon = \frac{1 - P_{Cl_2}}{1 - \frac{P_{Cl_2}}{2}} \quad (33)$$

If one or more of the substances E,  $E_aO_2$ , or  $E_aCl_4$  is gaseous at the chlorination temperature, the number of degrees of freedom in this system will be increased, and its thermodynamic analysis will be more complicated. Calculation of the equilibrium will require simultaneous solution of a system of equations expressing the equilibrium and mass-balance conditions and equality of the total system pressure to one atmosphere. If the reducing agent, and its oxide and chloride, are gaseous at the chlorination temperature, simultaneous solution of this equation system is most time-consuming. In this case, if Reactions (22a) and (22b) can be disregarded, we have the following equilibrium conditions:

$$\frac{P_{TiCl_4} \cdot P_{E_aO_2}}{P_E^2 \cdot P_{Cl_2}} = K_{21} \quad (34)$$

$$\frac{P_{E_aCl_4}}{P_E \cdot P_{Cl_2}} = K_{22} \quad (35)$$

where  $a_1$ ,  $a_2$ , and  $a_3$  are the numbers of molecules of the gaseous products  $E_aO_2$ , E, and  $E_aCl_4$ , respectively, that are formed or consumed in Reactions (21) and (22) for each two chlorine molecules.

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If the reducer is placed in the chlorinator in an amount that is stoichiometric with the chlorine, we have

$$a_2 P_{Cl_2} = 2b_2. \quad (36)$$

In addition,

$$a_1 P_{TiCl_4} = P_{E_2O_3} \quad (37)$$

$$P_{TiCl_4} + P_{E_2O_3} + P_{E_2Cl_4} + P_{Cl_2} = 1. \quad (38)$$

After determining the equilibrium partial pressures from this equation system, we found the equilibrium degree of utilization of the chlorine and the fraction of the amount of chlorine fed into the chlorinator that goes into the useful product,  $TiCl_4$ , under equilibrium conditions.

Much as in the preceding case, the degree of chlorine utilization

$$\epsilon = 1 - \frac{P_{Cl_2}}{P_{Cl_2}^0} = 1 - \frac{P_{Cl_2}}{P_{Cl_2} + 2P_{TiCl_4} + \frac{2}{a_2} P_{E_2Cl_4}} \quad (39)$$

$$\epsilon = 1 - \frac{P_{Cl_2}}{P_{Cl_2} + 2P_{TiCl_4} + \frac{2}{a_2} P_{E_2Cl_4}} \quad (40)$$

The fraction of chlorine that has gone into the  $TiCl_4$  under equilibrium conditions is

$$\epsilon_1 = \frac{2P_{TiCl_4}}{P_{Cl_2}} = \frac{2P_{TiCl_4}}{P_{Cl_2} + 2P_{TiCl_4} + \frac{2}{a_2} P_{E_2Cl_4}} \quad (41)$$

The ratio of the equilibrium partial pressures of  $TiCl_4$  and  $E_2Cl_4$  is determined by the equilibrium constant of the exchange reaction (29):

$$\frac{P_{TiCl_4} \cdot P_{E_2O_3}^0}{P_{E_2Cl_4}} = K_{29} \quad (42)$$

The smaller  $\Delta Z_{29}^0$ , the larger will be the equilibrium constant of this reaction and, consequently, the larger  $\epsilon_1$ .

The equilibrium of oxide-chloride exchange reactions such as (29) must also be taken into account in chlorinating multicomponent titanium raw materials with chlorine in the presence of carbon. The reactions between titanium tetrachloride and the oxide components of the raw material play an important role in the

processes taking place in the chlorinator zone in which there is practically no free chlorine. If the titanium tetrachloride partial pressure in the vapor-gas mixture is below the equilibrium pressure for Reaction (29), the chloride  $E_2Cl_4$  will become a chlorinating agent for the titanium dioxide, i.e., Reaction (29) will proceed from left to right. If, on the other hand, the titanium tetrachloride partial pressure is above the equilibrium for Reaction (29), the titanium tetrachloride will instead chlorinate the corresponding oxide, and the reaction will go from right to left.

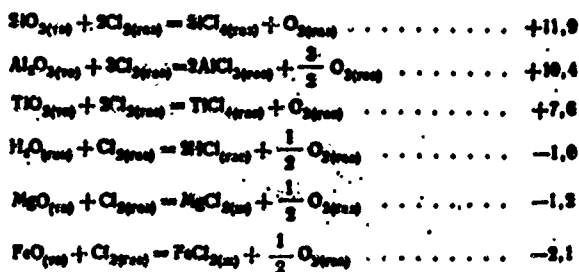
It is interesting to note that reactions of the (29) type can take place between an oxide and chloride of the same element, with formation of an oxichloride.

The equation of Reaction (29) can also be regarded as the difference between the equations of the reactions of chlorine with the corresponding oxides:



Consequently, the change in the standard isobaric potential of Reaction (29) equals the difference between the standard isobaric potential changes of these reactions. If  $\Delta Z_{43}^0 < \Delta Z_{44}^0$ , the equilibrium of the exchange reaction (29) is shifted toward the formation of  $E_1a_1Cl_4$ . If, however,  $\Delta Z_{10}^0 > \Delta Z_{11}^0$ , the equilibrium is shifted in favor of  $E_2a_2Cl_4$ .

The standard isobaric potential changes for the chlorination reactions of a number of oxides are given below for 1000°K in kcal/g-atom of Cl:



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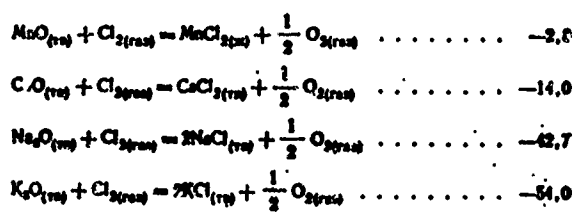
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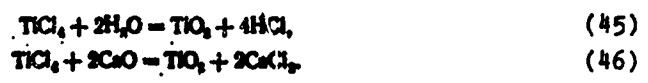
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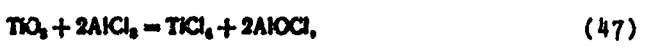


As we see from these data, the oxide components of the titanium raw material can be arrayed in the following series in order of their tendency to chlorination:  $\text{K}_2\text{O} > \text{Na}_2\text{O} > \text{CaO} > \text{MnO}, \text{FeO}, \text{MgO}, \text{H}_2\text{O} > \text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{SiO}_2$ . Since the chlorination process is controlled in such a way as to chlorinate the titanium dioxide as completely as possible, the oxides before  $\text{TiO}_2$  in the series are practically completely chlorinated. Aluminum and silicon oxides do not chlorinate as completely as titanium dioxide. Usually, the degree of their chlorination does not exceed 40%. As a result of the large drop of the standard isobaric potential, the chlorination reactions of the oxides of K, Na, and Ca have large equilibrium constants. Hence these oxides can be chlorinated by chlorine without a reducing agent. Efficient chlorination of the other oxides requires introduction of a reducer into the system.

As we noted above, the oxides and chlorides of the elements in this series can react with one another. Thus, for example, titanium tetrachloride can chlorinate oxides below it almost completely (see page 156-157):



The occurrence of such reactions between titanium tetrachloride and easily chlorinated oxides has been demonstrated experimentally [7, page 143; 46]. Schafer [38] showed that aluminum chloride is an active chlorinating agent for many oxides, including  $\text{TiO}_2$  even at comparatively low temperatures, but does not react with silicon dioxide. Under these conditions, the reaction of  $\text{TiO}_2$  with  $\text{AlCl}_3$  takes place with formation of aluminum oxychloride:



which is a white, practically nonvolatile solid. At temperatures above 600°C, it decomposes with formation of  $\text{AlCl}_3$  and  $\text{Al}_2\text{O}_3$ .

Chlorine compounds containing carbon and sulfur are also sometimes used as chlorinating agents to obtain titanium tetrachloride from the dioxide. Then the chlorination reactions proceed in accordance with the following over-all equations:



The equilibrium of each of these reactions has been shifted practically all the way to the right. However, note must be taken of the following. If the chlorination is conducted at temperatures at which the chlorinating agents are thermodynamically stable with respect to dissociation into reducer and chlorine molecules (the  $\Delta Z^\circ$  of formation of the chlorinating agent from the reducer and chlorine  $< 0$ ), the drop in the standard isobaric potential of Reactions (48-50) will be smaller than that for chlorination reactions of the (21) type.

In such cases, the equilibrium constant of the reactions in which chlorination is by chlorine compounds is smaller than that of the chlorine-chlorination reaction in the presence of an appropriate reducing agent. In practice, however, there are frequent cases in which the use of chlorine compounds instead of a mixture of chlorine with an appropriate reducer makes it possible to raise chlorinator productivity substantially and increase the degree of chlorine utilization. This is because the indicators of the process are determined under these conditions by kinetic factors rather than by thermodynamic equilibrium conditions. Thus, for example, Reaction (48) advances at considerable speed at 450°C, while the mixture of chlorine and carbon monoxide shows practically no reaction with titanium dioxide at these temperatures.

As we noted in Part II, the titanium in the slags is not only in the quadrivalent state, but also in the tri- and even the divalent states. Unlike titanium dioxide, the lower oxides may react directly with chlorine in the absence of a reducer, in

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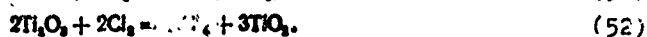
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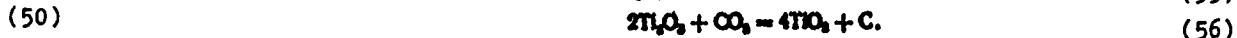
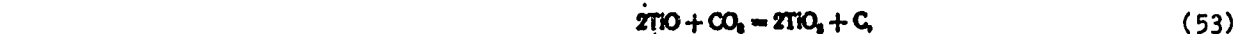
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In addition, the lower titanium oxides may be oxidized by carbon-containing gases:



The standard isobaric potential changes for Reaction (51-55) at 1000°K are -131, -107, -66.9, -34.0, and -20.5 kcal, respectively. The large loss of standard isobaric potential for Reactions (51) and (52) makes it possible to bind practically all of the chlorine. In chlorinating titanium monoxide in the presence of carbon, the ratio of the CO and CO<sub>2</sub> concentrations in the exhaust gases is higher than in titanium dioxide chlorination [45]. This may be explained by the occurrence of Reaction (54). Leaving kinetic factors aside, we may state that the lower oxides of titanium will be chlorinated more actively than the dioxide when Reactions (53) and (56) proceed from left to right. In this case, the TiO and Ti<sub>2</sub>O<sub>3</sub> phases will be thermodynamically unstable with respect to the TiO<sub>2</sub>-carbon mixture.

#### Mechanism and Kinetics of Chlorination

Little study has been devoted to the mechanism by which metal oxides are chlorinated by chlorine in the presence of carbon. The prevailing conceptions of the chlorination mechanism as it applies to titanium dioxide can be broken down into the following groups.

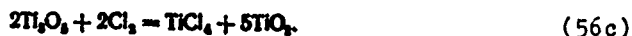
First group [10, 46, 47]. The chlorine reacts with titanium dioxide by Reaction (9), with formation of titanium tetrachloride and elementary oxygen, which then combined with the carbon to form CO<sub>2</sub> or CO by reactions (12) and (12a).

Second group [12, 13, 46]. The titanium dioxide is first reduced by C or CO to a lower oxide:

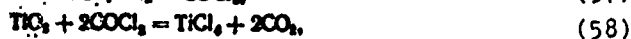




This oxide then reacts with the chlorine by Eq. (52) and forms  $\text{TiCl}_4$ ; an alternative is the reaction



Third group [15; 7, page 115; 48; 49]. The titanium dioxide is chlorinated by phosgene formed as a result of the reaction of chlorine with carbon monoxide in the presence of carbon:



Fourth group [15, 49, 50, 51]. Chlorination is effected by chlorocarbons formed on the surface of the carbon.

Fifth group [7, page 135; 14, 15]. Chlorination proceeds via an intermediate stage in which radicals whose molecules contain oxygen are formed. The process takes place in the absence of direct contact between the titanium dioxide and carbon particles.

We ran experiments to test the first three groups, whose schemes have been formulated in quite specific terms. Coked briquettes made from a mixture of rutilized titanium dioxide and lampblack were subjected to chlorination. A 40% solution of sugar in water was used as a binder. The briquettes contained 24% carbon.

It was established from study of the rate of chlorination by a chlorine-oxygen mixture at low temperatures, when there is no diffusive stagnation in the gas stream or in the pores between briquette particles, that the observed titanium tetrachloride vapor concentration in these pores was 7-9 orders higher than the equilibrium concentration for Reaction (9). This does not imply incompatibility of the first variant of the titanium dioxide chlorination mechanism with the experimental data. Comparison of the chlorination rates of briquettes made from a titanium-dioxide-lampblack mixture with the rate of reaction of lampblack briquettes with oxygen indicated that the latter process is

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(56b) slower. This fact indicates that the reaction of oxygen with carbon cannot be a stage in the chlorination process.

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(56c) The inconsistency in the hypotheses to the effect that the chlorination process passes through a stage in which titanium dioxide is reduced results from the following circumstances.

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tion of  
(57) It was established in a special experiment that  $\text{CO}_2$ , the  
(58) basic carbon-containing chlorination product of mixed titanium  
(20) dioxide and lampblack briquettes, is formed at  $400^\circ\text{C}$  as a direct  
result of the chlorination reaction, and is not a product of the  
secondary reaction  $2\text{CO} = \text{CO}_2 + \text{C}$ . During chlorination of a bed  
of briquettes, the  $\text{CO}_2$  partial pressure in the gas current is of  
the order of tenths of an atmosphere. Therefore, as a thermodynamic  
calculation indicates, intermediate chlorination products  
( $\text{Ti}_2\text{O}_3$  or  $\text{Ti}_3\text{O}_5$ ) cannot be isolated as a separate phase. If, on  
the other hand,  $\text{Ti}_2\text{O}_3$  or  $\text{Ti}_3\text{O}_5$  is present in the form of a solid  
solution in titanium dioxide, their activity in this solution  
may not exceed the equilibrium activity

$$\frac{a_{\text{TiO}_2}}{a_{\text{Ti}_2\text{O}_3}} = \left( \frac{K}{A_{\text{CO}_2}} \right)^{1/2} \quad (59)$$

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where  $K$  is the equilibrium constant of the reduction reaction (56a) or (56b);  $a_{\text{Ti}_2\text{O}_3}$  ( $a_{\text{Ti}_3\text{O}_5}$ ) is the equilibrium activity of  $\text{Ti}_2\text{O}_3$  ( $\text{Ti}_3\text{O}_5$ ) in the solid solution (the activity of  $\text{TiO}_2$  in this solution is assumed equal to unity).

If, during chlorination, the reduction reaction is catalyzed by the chlorine or by chlorination products and is close to equilibrium (the rapid stage), the rate of the chlorination process should decline with diminishing equilibrium activity of the  $\text{Ti}_2\text{O}_3$  ( $\text{Ti}_3\text{O}_5$ ) as the  $\text{CO}_2$  concentration in the gas stream rises. However, experiments conducted in the kinetic region of the chlorination process indicated that an increase in the carbon dioxide content in the gas stream from 10 to 80% had practically no effect on chlorination rate. Consequently, the reduction reaction cannot be the rapid stage of the chlorination process. If, however, this stage is not catalyzed during chlorination and is far from equilibrium, the inhibiting action of its products can be disregarded.

In this case, the observed chlorination rate should be about equal to the rate of the reduction reaction in the forward direction. But the latter, even at temperatures around 1000°C, is much lower than the observed rate of the chlorination reaction at 400°C. Hence the chlorination mechanism involving a reduction stage is not confirmed.

The authors of [52] cite the following facts in support of passage of chlorination through a stage in which phosgene is formed:

a) the activation energies for chlorination of rutile by phosgene ( $\sqrt{22}$  kcal/mole) and chlorine in the presence of carbon are closely similar;

b) the rates of chlorination of pyrochlore by chlorine in the presence of carbon and of niobium pentoxide by phosgene at 320°C are approximately equal.

Bergholm [14] offers a critique of the mechanism in which phosgene acts as a chlorinating agent in the process. He remarks that, as was established by Dunn [16], the reaction rate vs. temperature curve for the chlorination of rutile by phosgene has a minimum resulting from thermal dissociation of the phosgene.

In chlorination by chlorine in the presence of carbon, on the other hand, this curve does not have the minimum, and therefore indicates a different mechanism for the process.

Moreover, Bergholm showed in his own experiments that the addition of carbon monoxide to chlorine at 600°C has no influence on the rate of chlorination despite the fact that the phosgene concentration in the chlorinator should be higher in this case as a result of the reaction



The authors secured supplementary data to test this variant of the chlorination mechanism. It was shown that the rate of phosgene chlorination of briquettes made from mixed titanium dioxide and carbon, referred to unit mass of chlorinated dioxide, is lower than in chlorination of the same briquettes by chlorine at

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418-456°C (the kinetic region). These results also indicate the inconsistency of this mechanism for chlorination of titanium by phosgene, since the rate of the overall process (chlorination by chlorine in the presence of carbon) cannot exceed the rate of any single stage (chlorination by phosgene).

A number of authors have studied the kinetics of the chlorination of titanium slags and titanium dioxide. V.A. Reznichenko and V.P. Solomakha established that at 700°C, the rate of chlorination of briquettes made from mixed titanium dioxide and carbon is determined principally by the rates of diffusion processes [7, page 115]. At this temperature, in their opinion, the best ways to step up the chlorination process would be to raise the velocity of the gas stream and increase the exposed surface area of the particles to be chlorinated. In a study of the chlorination kinetics of a mixture of titanium dioxide and carbon powders suspended in fused chlorides, Kim Meng Ring and B.P. Melent'yev found that the optimum chlorination temperature was about 900°C. Below 800°C, the reaction rate drops sharply in accordance with the 11.1-kcal activation-energy value [7, page 120]. The authors assume that the melt is merely an inert medium for the process and that its components do not participate in the chlorination reaction. However, A.B. Bezukladnikov and Ya.Ye. Vil'nyanskly [7, page 135] showed that the chlorination rate of titanium dioxide is several times higher when small amounts of iron and aluminum chlorides are added to fused carnallite. In chlorination of titanium dioxide in pure fused carnallite, the chlorination process is characterized by an activation energy of 11.2 kcal/mole right up to 900°C. The addition of 2% ferric chloride to the carnallite transfers the chlorination process into the diffusion region at a temperature of about 680°C (activation energy ~0.7 kcal/mole). In a study of the chlorination kinetics of titanium slags in fused chlorides, P.P. Khomyakov found that increasing the FeO and CaO contents in the titanium slags to 10 and 6%, respectively, gives a substantial increase in the rate of the process. Increasing the FeCl<sub>2</sub> content in the melt to 11-12% produces the same result. The process rate is adversely influenced by increasing the CaCl<sub>2</sub> content in the melt to 10%. The optimum KCl-MgCl<sub>2</sub> ratio in the

melt is closely similar to their proportions in natural carnallite [31].

In a study of the chlorination of titanium monoxide, A.N. Zelikman and T. Segarchanu [53] established that, in contrast to the dioxide, it chlorinates quite rapidly at 300°C without carbon. In the 400-700°C temperature range, the maximum degree of chlorination of the titanium is 50%, because the reaction takes the course of Eq. (51). The authors established that in the presence of carbon at 500°C, titanium monoxide is 97% chlorinated, while the maximum chlorination of titanium dioxide under the same conditions does not exceed 50%. The explanation offered by the authors for this result is that the monoxide chlorination process passes through a stage in which titanium dioxide is formed. This dioxide is chemically active and practically all of it is chlorinated in the presence of carbon at 500°C. V.A. Reznichenko and V.P. Solomakha [45], who studied the chlorination of titanium monoxide, confirmed the research results of A.L. Zelikman and T. Segarchanu that were set forth above as to the influence of temperature on the relative chlorination rates of  $TiO$  and  $TiO_2$ . Like those authors, they conclude that the chlorination of titanium monoxide in the presence of carbon proceeds via the formation of  $TiO_2$  as an intermediate product. As we noted, they established the interesting fact that the  $CO/CO_2$  ratio in the exhaust gases at temperatures up to 800°C is higher in the chlorination of titanium monoxide in the presence of carbon than in the chlorination of the dioxide.

In another study, V.A. Reznichenko and V.P. Solomakha [7, page 102] studied the chlorination of titanium slags with various contents of lower titanium oxides. The authors concluded that the presence of the lower oxides lowers the chlorination rates of the titanium slags and raises the carbon monoxide content in the exhaust gases. On the other hand, the presence of calcium and magnesium oxides accelerates slag chlorination. However, it had been established earlier [53] that the chlorination rate of titanium oxide in the presence of carbon is higher at low temperatures than the chlorination rate of the dioxide. At high temperatures (in

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the diffusion region), on the other hand, the chlorination rates of these oxides should be determined by the diffusion rate of chlorine to the unreacted briquette surface. This rate does not depend on the chemical properties of the chlorinating agent, and is determined by geometrical relationships and the physical properties of the gas stream and the chlorination residue surrounding the reaction zone. For this reason, the authors' conclusion to the effect that the lower oxides have a detrimental influence on slag chlorination rate appears doubtful. The experimental data on which this conclusion was based cannot be regarded as indicating it without ambiguity, since the paper gives no information on the reproducibility error of the experimental results.

We should accordingly expect the presence of lower titanium oxides to activate chlorination at the low temperatures corresponding to the kinetic or internal-diffusion region of the process. At high temperatures (external diffusion region), however, the chlorination rates of titanium slags containing various amounts of the lower oxides would be determined by the properties of the chlorination residue, through which chlorine diffuses to the reaction zone, or by the rate of chlorine arrival at the outer surface of the briquette.

S.L. Stefanyuk and I.S. Morozov [52] established that the chlorination of loparite, zircon, euxenite, and pyrochlore crystals in the presence of carbon at 550-1080°C may be regarded as taking place on the geometric surface of the crystal. The rates of advance of all points of the reaction front toward the center of the crystal are the same, do not depend on the degree of its chlorination, and are subject to the Arrhenius equation:

$$k_p = A e^{-\frac{\epsilon}{RT}}, \quad (60)$$

where  $\epsilon$  is the activation energy of the process and  $k_p$  is the rate of displacement of the reaction front.

The minerals listed above have  $\epsilon$  ranging from 23.3 to 25.8 kcal/mole and widely varying multipliers before the exponential.

After studying the chlorination kinetics of loparite and pyrochlore, the same authors [55] established that the chlorination

of a spherical briquette made from a mixture of concentrate with carbon localizes in a narrow zone in the diffusion region of the chlorination process. The rate at which this zone moves toward the center as the briquette is chlorinated does not remain constant. As a time function, the depth of the chlorinated zone is described by the empirical equation

$$x = k\tau^m, \quad (61)$$

where  $x$  is the depth of the chlorinated zone,  $k$  and  $m$  are constants, and  $\tau$  is the time elapsed from the start of chlorination.

The order of the chlorination reaction with respect to chlorine is fractional (0.5 for loparite concentrate and 0.8 for the pyrochlore concentrate). The authors suggest the following formula for rough calculation of briquette-chlorination depth for a mixture of loparite concentrate and carbon:

$$Z = \frac{3\sqrt{3}}{\pi} \cdot \frac{\Pi}{\gamma_0} \left( \frac{R_0}{k} \right)^{\frac{1}{m}}, \quad (62)$$

where  $Z$  is the depth of the chlorination zone,  $\Pi$  is the specific productivity of the chlorinator,  $R_0$  is the briquette initial radius, and  $\gamma_0$  is the density of the briquette.

However, Formula (62) does not reflect the influence exerted on the chlorination process by such factors as the chlorine contents in the supply and exhaust gases, the rates of motion of the briquettes and the chlorine in the chlorinator, the manner in which they move (forward or countercurrent), or the degree of chlorination of the concentrate at the exit from the reaction zone.

We studied the low-temperature chlorination rates of small briquettes made from a mixture of titanium dioxide with lampblack. A 40% sugar solution was used as a binder. It was shown that chlorination proceeds uniformly throughout the entire volume of the briquette. The chlorination rate is proportional throughout the entire process to the "active mass" of the briquette, and is expressed by the equation

$$w' = \frac{dx}{dt} = k'(x_m - x), \quad (63)$$

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where  $w'$  is the instantaneous chlorination rate of the titanium dioxide throughout the volume of the briquette,  $x_{\infty}$  is the amount of titanium dioxide that has been chlorinated when the process has come to a complete stop (for an unlimited time of the experiment),  $x_t$  is the amount of titanium dioxide that has been chlorinated at time  $t$ , and  $k''$  is a coefficient that does not depend on the degree of chlorination of the briquette and is of the nature of a rate constant.

Integration of this equation yields

$$\ln\left(1 - \frac{x_t}{x_{\infty}}\right) = -k''t \quad (64)$$

The experimental data are presented in Figs. 26 and 27.

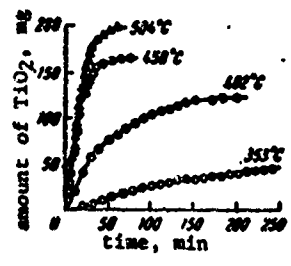


Figure 26. Amount of chlorinated titanium dioxide as a function of time and temperature.

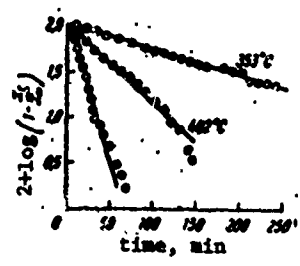


Figure 27. Chlorination of a briquette made from a mixture of titanium dioxide and carbon in the kinetic region.

As we see from Fig. 27, this last equation agrees satisfactorily with experiment up to 458°C.

The chlorination reaction is a heterogeneous process. Its rate should be proportional to the particle surface area on which the reaction unfolds. But for a porous briquette in the absence of diffusion retardation in the pores between particles, this area is proportional to the volume of the briquette and, consequently, to its mass. This explains the proportionality noted earlier between chlorination rate and briquette mass. On this basis, the

expression for chlorination rate can be rewritten

$$w' = k'(x_{\infty} - x) = k'S'_0(x_{\infty} - x), \quad (65)$$

where  $S'_0$  is the total area of the pores in the briquette per unit briquette mass at time zero.

Relating the reaction rate to briquette unit volume, we obtain

$$w = \frac{w'}{V} = \frac{k'S'_0(x_{\infty} - x)}{\frac{x_0}{\rho_0}}, \quad (66)$$

where  $x_0$  is the mass of the briquette before the start of chlorination and  $\rho_0$  is the density of the briquette.

If the proportions of titanium dioxide and carbon in the briquette are near stoichiometric, the proportions of the components does not change in the course of the reaction, and the mass of the briquette is proportional to the amount of titanium dioxide present in it. Therefore,

$$w = k'S_0(\epsilon_{\infty} - \epsilon),$$

where  $S_0$  is the total initial surface area of the pores in the briquette per unit briquette volume,  $\epsilon_{\infty}$  is the maximum degree of chlorination of the titanium dioxide, and  $\epsilon$  is the degree of chlorination of the titanium dioxide at the particular point in time.

We have  $\epsilon_{\infty} = \text{const}$  at a given carbon content in the briquette and constant temperature. Further studies showed that the initial expression for the rate of the process also remains valid for chlorination of uncoked briquettes prepared by pressing titanium dioxide powder with lampblack without the addition of a binder. In this case, however, chlorination proceeds apace at a higher temperature. This is because of the higher chemical activity of the carbon formed on thermal decomposition of the sugar in the coking process as compared with lampblack.

It was also found that chlorination rate is proportional to about the 0.5 power of chlorine concentration in the gas stream. Thus, we have finally

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$$w = kS_p(c_{\infty} - c)C_{Cl_2}^0 \quad (67)$$

(65) where  $C_{Cl_2}$  is the chlorine concentration in the pores between particles. In the absence of diffusion retardation, it is practically equal to the chlorine concentration in the gas stream. With these data as a basis, let us scrutinize the chlorination kinetics of briquettes made from a mixture of titanium concentrate with carbon. Chlorination of briquettes is a complex heterogeneous process that passes through the following principal stages:

- a) convective diffusion of chlorine to the outer surface of the briquette;
- b) molecular diffusion of chlorine into the briquette through the pores between particles;
- c) chemical reaction between the chlorine, the titanium concentrate, and the carbon.

The first process is governed by molecular diffusion of the chlorine and its transport to the briquette surface as a result of motion of the gases in the chlorinator. As a rule, it is still impossible to calculate the theoretical chlorine flow to the outer surface of the briquette as it is governed by these two transport mechanisms. It is therefore advisable to use empirical relationships obtained by dimensional analysis.

Let us isolate all quantities that control the rate of supply of chlorine from the gas stream to the outer surface of the briquette, all zones of which will be considered equally accessible by diffusion. We shall characterize the rate of chlorine supply by the mass-transport coefficient  $\beta$  ( $\beta$  is the amount of chlorine arriving at a unit surface area of the briquette from the gas stream per unit time at unit chlorine-concentration difference between the main gas flow and the briquette surface). In the steady state, therefore, the flow of chlorine to the outer surface of the briquette will be expressed by the equation

$$\Pi = \beta(C_g - C_0)F_0 \quad (68)$$

where  $C_g$  and  $C_0$  are the chlorine concentrations in the gas stream

and on the briquette outer surface, respectively, and  $\Sigma_0$  is the outer-surface area of the briquette.

Obviously, the mass-transport coefficient depends on the average velocity  $\underline{v}$  of the gas flow in a cross section of the chlorinator, on the briquette size  $\underline{d}$ , on the diffusion coefficient  $D$  of the chlorine, and gas density  $\rho$ , and the viscosity  $\eta$  of the gas:

$$\beta = f(v, d, D, \eta, \rho). \quad (69)$$

The total number of quantities related by this equation is 6. We can easily satisfy ourselves that 3 of them have independent dimensions. According to the  $\pi$  theorem, therefore, the relationship among them can be represented in the form of a relationship linking three dimensionless combinations composed of these six quantities:  $\pi_1 = F(\pi_2, \pi_3)$ . In principle, any dimensionless combinations written independently of one another may be used. In this case, however, it is advantageous to use the combinations

$$\pi_1 = Nu = \frac{\beta d}{D}; \quad \pi_2 = Re = \frac{\rho v d}{\eta}; \quad \pi_3 = Pr = \frac{\eta}{D \rho}.$$

The first of these is the Nusselt number, the second the Reynolds number, and the third the Prandtl number.

Consequently,  $Nu = F(Re, Pr)$ . Since  $Pr = 1$  for ideal gases, we have  $Nu = F(Re)$ . Having determined the form of this relationship from experimental data, we can calculate  $\beta = NuD/d$  and the chlorine flow to the briquette outer surface

$$\Pi = \frac{NuD}{d} (C_s - C_0) \Sigma_0. \quad (70)$$

The chlorine molecules diffuse through pores from the outer surface into the interior of the briquette. The diffusion process is accompanied by chemical reaction, with the result that a chlorination zone with a certain extent into the depth of the briquette is formed. With time, the chlorination zone moves away from the outer surface toward the center of the briquette. Its place is taken by an unchlorinated "cinder" zone that does not react with the chlorine. To evaluate the extent of the chlorination zone into the depth of the briquette for various conditions

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of the process, we shall call upon the results of Ya.D. Zel'dovich [11], who analyzed diffusion in pores that is accompanied by chemical reaction. Although the chemical reaction takes place on the surface of the titanium-concentrate and carbon particles, its rate can be related to a unit volume of the briquette by regarding the briquette as a homogeneous solid.

In this case, we can write the following chlorine mass balance equation for an infinitesimally small volume of the chlorination zone in the neighborhood of the point under consideration:

$$\frac{\partial C}{\partial t} = D' \Delta C - w. \quad (71)$$

If, in accordance with the above, we take  $w = kS_0(c_{\infty} - c)C^n$ , we have

$$\frac{\partial C}{\partial t} = D' \Delta C - kS_0(c_{\infty} - c)C^n, \quad (72)$$

where  $C$  is the chlorine concentration at the particular point in the briquette,  $t$  is time,  $\Delta$  is the Laplacian operator,  $n$  is the order of the reaction with respect to the chlorine, and  $D'$  is the effective coefficient of chlorine diffusion in the briquette, which is assumed constant.

Considering that the rate of accumulation of chlorine at the particular point is negligibly small by comparison with the reaction rate, we obtain

$$\frac{\partial C}{\partial t} = 0 \text{ and } D' \Delta C = kS_0(c_{\infty} - c)C^n. \quad (73)$$

If the dimensions of the briquette are very large by comparison with the depth of the chlorination zone, the chlorination-zone layer may be assumed planar. In this case,  $\Delta C = d^2C/dx^2$ , where  $x$  is the distance of the particular point from the outer surface of the briquette.

At time zero,  $c = 0$  for chlorination of a "fresh" briquette. At  $x = \infty$ ,  $C = 0$  and  $dC/dx = 0$ . With these conditions, integration of (73) yields

$$\frac{dC}{dx} = -\sqrt{\frac{2}{n+1} \cdot \frac{kS_0 c_{\infty}^{n+1}}{D'}} C^{\frac{n+1}{2}}; \quad (74)$$

$$C = C_0 \left( \frac{n-1}{\sqrt{2(n+1)}} x \sqrt{\frac{kS_0 \epsilon_0 C_0^{n-1}}{D'}} + 1 \right)^{\frac{2}{1-n}} \quad \text{for } n \neq 1 \quad (75)$$

and

$$C = C_0 e^{-\sqrt{\frac{kS_0 \epsilon_0 C_0^{n-1}}{D'}} x} \quad \text{for } n = 1. \quad (76)$$

For a briquette made from a mixture of titanium dioxide with lampblack,  $n = 0.5$ , and the chlorination-zone depth is determined by Expression (75). The chlorine concentration becomes zero at a distance of  $x_0 = 2\sqrt{3} \sqrt{\frac{D'}{kS_0 \epsilon_0 C_0^{n-1}}}$  from the briquette outer surface, i.e., the chlorination zone is of finite extent. If  $n \geq 1$ , the chlorine concentration vanishes only at  $x = \infty$ . For  $n = 1$ , the chlorine concentration diminishes by a factor of  $e$  as the distance from the briquette outer surface increases by an amount  $\sqrt{\frac{D'}{kS_0 \epsilon_0}}$ .

It is convenient to take  $L = \sqrt{\frac{D'}{kS_0 \epsilon_0 C_0^{n-1}}}$  as the unit of measurement for distance from the briquette outer surface. In practice, the chlorine concentration will be negligibly low at  $x \approx 3L$  by comparison by its concentration at the briquette outer surface. If the briquette size greatly exceeds this length, the chlorination-zone layer may be regarded as planar and the relationships derived above can be used for briquettes of arbitrary shape. For low enough temperatures, the depth of the chlorination zone far exceeds the briquette radius:  $L \gg r$ . In this case, the chlorine concentration will be practically uniform throughout the volume of the briquette, and the rate of the chlorination process will be proportional to briquette volume. With rising temperature, the rate constant of the chemical reaction will rise much more rapidly than the diffusion coefficient.  $L$  will therefore become smaller. Consequently, the finer the briquettes, other conditions the same, the higher will be the temperature at which the chlorination process still takes place throughout the entire volume of the briquette (the kinetic region). The influence of diffusion retardation on chlorination rate begins to make itself felt only after

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(75) the depth of the chlorination zone has become of the order of the briquette radius. With further temperature increase, the extent of the reaction zone will continue to diminish.

(76) When the chlorination-zone depth has become much smaller than the briquette radius, but is still much larger than the radius of the briquette's pores, the chlorination process will follow Eqs. (74) and (75) or (76) in the internal-diffusion region.

The reaction rate will then be proportional to the external surface area of the briquette.

The amount of chlorine that reacts in the briquette per unit time under steady-state conditions equals the total chlorine flow across the outer surface of the briquette:

$$\Pi = -D' \left( \frac{dC}{dx} \right)_{x=0} S_p \quad (77)$$

Substituting the value of  $dC/dx$  from Eq. (74) into this expression, we get

$$\Pi = \sqrt{\frac{2}{n+1} k D' S_p c_0^{\frac{n+1}{2}} E_0} = \lambda C_0^{\frac{n+1}{2}} E_0 \quad (78)$$

If the process is not limited to the stage of external mass transport, the chlorine concentration at the briquette outer surface will be approximately equal to the chlorine concentration in the gas stream. This last value is practically independent of temperature, and  $\lambda$  may be regarded as the effective rate constant of the process. Then, disregarding the dependence of  $c_0$  on temperature, we obtain according to the Arrhenius equation

$$\frac{d \ln \lambda}{dT} = \frac{E}{RT^2} = \frac{1}{2} \cdot \frac{d(\ln \lambda + \ln D')}{dT} = \frac{1}{2RT^2} (E_p + E_d), \quad (79)$$

where  $E$  is the observed process activation energy,  $E_p$  is the activation energy of the chemical reaction, and  $E_d$  is the activation energy of diffusion. Hence

$$E = \frac{1}{2} (E_p + E_d) \approx \frac{E_p}{2}, \quad (80)$$

i.e., the activation energy of the process in the internal-diffusion region is in practice half the activation energy of the

chemical reaction.<sup>(1)</sup>

If the temperature continues to rise, the depth of the chlorination zone will diminish until it is of the order of the briquette pore diameter, and there will be no further narrowing of the reaction zone thereafter. Chlorination will proceed in a thin layer just below the briquette outer surface, and the above equations will cease to apply. Beyond that point, the manner in which chlorination rate depends on temperature will be determined by the relation between the external mass transport coefficient and the chemical-reaction rate constant  $k_1$  referred to a unit external surface area of the briquette. If  $\beta > k_1 C_p^{-1}$ , the chlorination of the briquette will again shift into the kinetic region. The process activation energy will then again become equal to the chemical reaction activation energy  $E_p$ . If  $\beta < k_1 C_p^{-1}$ , the process is transferred into the external-diffusion region. If  $\beta \ll \frac{D'}{r}$ ; rising temperature will throw the chlorination process into the external-diffusion region directly from the kinetic region, without passing through the internal-diffusion region with activation energy  $E_p/2$ .

This effect should arise in chlorination of briquettes in an industrial chlorinator if the chlorination zone envelops the cinder layer, which offers substantial resistance to diffusion.

Let us consider the case in which the chlorination reaction takes place in a narrow zone at the outer surface of the unchlorinated part of the briquette. Let the rate of the process be limited by the stage in which chlorine is brought up to the briquette outer surface and the stage of diffusion of the chlorine through a cinder layer enveloping the unchlorinated part of the briquette. If the briquette outer surface is uniformly accessible, the cinder is physically homogeneous, and its formation does not change the total volume of the briquette, we have the differential equation  $D''AC = 0$ , where  $D''$  is the effective coefficient of diffusion of chlorine through the cinder layer, in steady-state chlorination for any point of the "cinder" zone instead of Eq. (73). Integration of this equation for a spherical briquette with consideration of the conditions formulated above and equality of Footnote (1) appears on page 190.

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the convective chlorine flow to the briquette outer surface to the diffusive flow of chlorine from this surface across the cinder layer gives the following relationship for the radius of the unchlorinated part of the briquette as a function of time:

$$\frac{D'' \rho_0 C_{Cl} t}{\rho_0 v r_0^2} = \beta \left( \frac{1-x^2}{2} \right) + \left( \frac{D''}{r_0} - \beta \right) \left( \frac{1-x^2}{3} \right), \quad (81)$$

where  $t$  is the chlorination time,  $r_0$  is the radius of the briquette,  $x$  is the ratio of the radius of the unchlorinated part of the briquette to the radius of the briquette,  $v$  is a coefficient that establishes the relation between the amounts of chlorinated concentrate and reacted chlorine and can be determined from the stoichiometric coefficients of the chlorination-reaction equations of the concentrate components, and  $\rho_0$  is the content of concentrate per unit volume of the unchlorinated part of the briquette.

It was assumed in integrating the differential equations given above that the temperature of the briquette is constant throughout its mass and equal to the temperature of the gas stream. This condition is not ordinarily met in reality because of the exothermic nature of the chlorination reaction of titanium concentrate. However, when small briquettes are chlorinated in the low-temperature range (kinetic region), in which case the reaction rate is very low, the heat liberated can dissipate, and this condition may therefore be regarded as approximately valid. If chlorination takes place in the diffusion region, the difference between the temperatures at different points in the briquette and the gas stream may be quite substantial. However, it appears that this circumstance is not an important factor, since the values of  $\beta$  and  $D''$ , which determine the rate of the reaction in the diffusion region, depend little on temperature. We have also disregarded the possible influence of Stefan flow and thermal diffusion on the kinetics of the process in the diffusion region.

#### Methods of Producing Titanium Tetrachloride

Several methods for the production of titanium tetrachloride are now known. However, the acknowledged industrial methods are chlorination of briquettes consisting of a mixture of titanium

slag or concentrate with coke and chlorination of a mixture of powdered slag or concentrate and coke suspended in a chloride melt.

Among the methods that have not yet come into extensive industrial use, we should note first of all fluidized-bed chlorination. This is a highly productive process. However, its application for chlorination of titanium slags encounters serious difficulties. Formation of the high-boiling fusible chlorides  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{NaCl}$ , and others causes the particles of the charge to stick together, and this disrupts the fluidized bed. This, in turn, disturbs the operation of the equipment and forces shutdown of the chlorination process. The attempt to eliminate melt formation by lowering the chlorination temperature to  $600^\circ\text{C}$  and below failed because chlorination does not proceed rapidly enough at these temperatures [32]. The literature makes reference to the possibility of binding the calcium oxide into an infusible phosphate with the aid of titanium phosphate.<sup>(2)</sup> Another countermeasure against coalescence of the fluidized particles of the charge is to raise the chlorination temperature to  $1300^\circ\text{C}$ .<sup>(3)</sup> The alkali- and alkaline-earth-metal chlorides are then driven out of the chlorinator in vapor form.

Overheating in certain parts of the reaction zone has sometimes been observed during processing of concentrates with high titanium contents. To disperse the liberated heat throughout the volume of the chlorinator, chlorination is sometimes carried out in the presence of particles of an inert substance that lowers the reaction-zone concentration of the material to be chlorinated.

In a variety of fluidized-bed chlorination of titanium raw material, the bed is used to produce a rutile concentrate from ilmenite. The reactor has two stages. In the first stage, the ilmenite is oxidized and the  $\text{FeO}$  is converted to  $\text{Fe}_2\text{O}_3$  to prevent the formation of  $\text{FeCl}_2$  during chlorination. The ferric oxide is chlorinated in the second stage. The chlorination product, titanium dioxide, is obtained in the rutile form [33]. Natural rutile and titanium dioxide chlorinate well in the fluidized bed.

Footnotes (2) and (3) appear on page 190.

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Interest attaches to chlorination of titanium dioxide in a fluidized bed of small porcelain balls of known granulometric composition. This bed is fed with a charge of  $\text{TiO}_2$  and coke together with the chlorine in a fuming process, or with titanium dioxide and a mixture of chlorine and carbon monoxide. The inert granulated bed reduces dusting substantially. The method can therefore be used to chlorinate extremely fine-grained materials without first granulating them [34].

A method that may eventually become attractive is fluidized-bed chlorination of rutile concentrates, which contain, depending on the concentration method, either 45-55%  $\text{TiO}_2$  (flotation concentrate) or 80%  $\text{TiO}_2$  (autoclave concentrate) and, respectively, 35-40 and 3-4% silicon dioxide, with the remainder composed basically of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  impurities. The concentrates do not contain substantial amounts of the impurities, which form fusible chlorides.

Chlorination of titanium-bearing materials (which have first been concentrated by the method used in chlorination of titanium slags) in a stationary packing or inert material has been studied on a laboratory scale [16]. The loose charge and chlorine are supplied at the top of the chlorinator. A grating carrying the packing (quartz, porcelain, etc.) is provided in the middle of the chlorinator. The stack for offtake of the vapor-gas mixture leaves the column below packing level. The resulting fusable reaction products drain through the packing and accumulate at the bottom of the chlorinator. The part played by the packing in this process was not studied. It may be assumed that it serves to increase the surface area on which chlorination develops.

There are a number of known methods for chlorination of titanium-containing materials using carbon monoxide as a reducing agent [35-37].

A mixture of chlorine and carbon monoxide was used as a chlorinating reagent in fluidized-bed chlorination of a stationary layer of briquettes and powdered titanium concentrate. The author of [16] studied the possibility of using phosgene as the chlorinating agent. Phosgene is a more active chlorinating agent at

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low temperatures than the mixture of CO and chlorine. The best results are obtained with phosgene at 690°C. As the temperature is raised further, the rate of chlorination declines because of decomposition of the phosgene. The worst results were obtained at 840°C. Above 840°C, the process picks up again, since the chlorinating agent is now a mixture of CO and Cl<sub>2</sub> formed by the decomposing phosgene.

A process of selective chlorination of titanium slag with a mixture of chlorine and hydrogen chloride for the production of high-titanium concentrate has also been described.<sup>(4)</sup>

Methods are known for the production of titanium tetrachloride by chlorination of the carbidization products of the titanium raw material. The starting raw material for acquisition of the carbides and their subsequent chlorination may be ilmenite, titanium slag, rutile, or titanium dioxide [56, 57].<sup>(5)</sup> Takimoto proposed that rutile be carbidized at 1800°C to lower the chlorination temperature to 300°C [41]. The Electromet company has a pilot plant at which ilmenite concentrate is carbidized in a resistance furnace. The resulting titanium oxycarbide is chlorinated at 400°C after magnetic separation of the iron to produce titanium tetrachloride [54].

Chlorination of carbides is accompanied by liberation of a large amount of heat. This process advances very rapidly even at comparatively low temperatures, and does not require expenditure of energy in heating the chlorinator.

Metal sulfides react quite vigorously with chlorine. The chlorination reaction of Me<sub>x</sub>S<sub>y</sub> takes place at high rates at relatively low temperatures (200-400°C).

Here the ilmenite concentrate is melted to a matte in a mixture with coke and pyrites. Smelting takes place at 1450-1500°C, i.e., at a temperature somewhat below that at which the same concentrates are smelted for slag. The resulting matte is chlorinated with chlorine at 750°C. The iron chlorides remain in the reaction zone, while the tetrachloride is distilled off to a condensation system.

Footnotes (4) and (5) appear on page 190.

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### Technology of Chlorination in an Electric Shaft Furnace

Figure 28 shows a flow chart of shaft-furnace chlorination. The process begins with preparation of the raw material for chlorination. To ensure uniform distribution of the gases over the chlorinator cross section and reduce the resistance offered by the material to be chlorinated to the passage of the gas current, the concentrate is mixed with carbon and briquetted. The titanium concentrate is first ground to an 80% content of the minus 0.10 mm fraction, and the petroleum coke to an 80% content of the minus 0.15 mm fraction. Grinding is necessary to increase the contact area of the reagents and to produce sufficiently strong briquettes. The ground materials are mixed with a binder in special paddle mixers [43, 44].

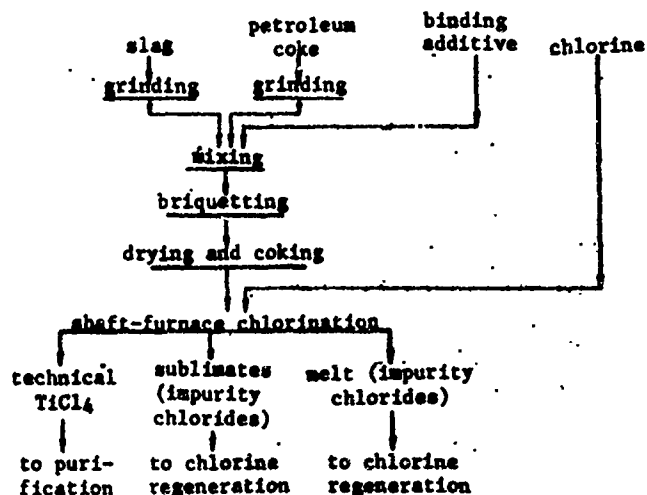


Figure 28. Flow chart of titanium tetrachloride production by chlorination of titanium slags in the form of a briquetted charge.

The binders used include coal-tar pitch, tar, concentrated sulfite-alcohol residues, etc. The amount of binder is selected as a function of the specific pressure to be used in briquetting at a given charge granulometric composition.

If roller presses that develop a pressure of 300 kgf/cm<sup>2</sup> are used for briquetting, the pitch content should be 7-8% of charge mass for charges preheated to 90°C, or 5-6% for preheating to 100-110°C.

If briquetting is done with roller-ring presses developing a pressure of 1000 kgf/cm<sup>2</sup>, the amount of binder can be reduced to 2-3%.

When sulfite-alcohol residue solution (density 1.27 g/cm<sup>3</sup>) is used as a binder, from 10 to 14% of it is added to the charge, depending on specific pressing pressure [32].

The raw briquettes are dried at about 120°C and coked to remove volatile substances, whose presence in the briquettes results in waste of chlorine, additional losses of titanium with the solid chlorides dumped from the condensation system, and contamination of the technical titanium tetrachloride by organic impurities.

The coking temperature depends basically on the type of binder added. For tar and pitch, volatile substances are eliminated practically completely from the briquettes at 800-850°C. If sulfite-alcohol residue is used as a binder, it is sufficient to coke at 500-600°C. To avoid cracking the briquettes, the temperature should be raised no faster than 100°C per hour during the coking process.

The coking time is usually 14 to 20 h. Coking can be carried out in intermittent or continuous furnaces. Furnaces of the former type, which are used when the scale of production is modest, include compartment kilns that are heated by burning a liquid or gaseous fuel in them. The continuous types, which are used for production on larger scales, include retort and tunnel furnaces.

A normal chlorination process in a shaft furnace requires that the briquettes meet certain requirements, and namely: their size and shape must be strictly uniform; the distribution of carbon through the volume of a briquette must be uniform; the briquette must have adequate strength; the strength of a briquette must be no lower than 120-100 kgf/cm<sup>2</sup>. Otherwise, the briquettes will break up as they are transported and loaded into the

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chlorinator. The carbon content in the finished briquettes is 17-20%.

A recently proposed method of continuous coking by burning natural gas in the bed of briquettes

represents a further development of the coking process. Air is also added to the natural gas in the amount necessary for combustion of the volatile hydrocarbons liberated during coking [42]. The basic advantages of this method are its continuity and high productivity and low equipment write-off. There have also been suggestions for the use of agglomeration instead of briquetting to lump the charge. The titanium slag is mixed with rutile and coke for this purpose. Partial melting of the slag causes the particles of the charge to coalesce.<sup>(6)</sup> However, agglomeration of titanium slag for subsequent chlorination has not yet come into use industrially.

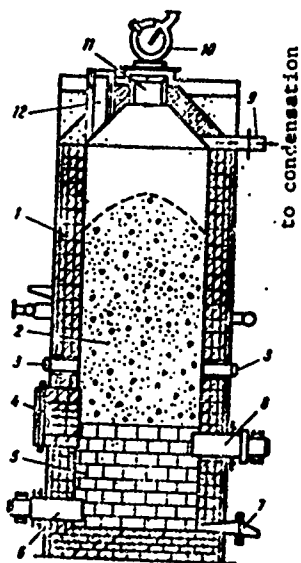


Figure 29. Diagram of shaft-electric-furnace-type chlorinator. 1) Lining; 2) briquettes; 3) chlorine supply; 4) manhole; 5) carbon packing; 6) lower-level electrode; 7) taphole; 8) upper-level electrode; 9) vapor-gas-mixture off-take pipe; 10) gate feeder; 11) charging hole; 12) emergency hatch.

The coked briquettes are conveyed in special containers to the furnace charging hoppers for chlorination. The briquettes are loaded into the furnace through a hole in the roof by a feeder sealed by a bell- or spool-type gate. The chlorine is fed into the furnace through tuyeres at the bottom.

The chlorinator (Fig. 29) can be discussed in terms of three levels. The lower zone (temperature below 700°C) is filled with the chlorination residue, which is richer in silica, aluminum oxide, and carbon than the initial briquettes. The basic components of this residue are as follows, in %: 20-40  $TiO_2$ , 1.5-2.0

Footnote (6) appears on page 190.

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Fe<sub>2</sub>O<sub>3</sub>, 4-5 Al<sub>2</sub>O<sub>3</sub>, 8-15 SiO<sub>2</sub>, 0.5-0.7 CaO, and 18-25 C.

The rather high contents of silica and aluminum oxide in the residue are accounted for by the low affinity of these oxides to chlorine. The high titanium dioxide and carbon contents in the residue apparently result from peculiarities of the mechanism by which the titanium dioxide is chlorinated. According to Berg-holm [14], rapid chlorination of titanium dioxide in the presence of carbon requires that the distance between the particles of these materials not exceed 0.2 mm. During the chlorination process, however, contact between the carbon and the concentrate is disturbed, and this lowers the reaction rate and causes titanium dioxide and carbon to appear in the unchlorinated residue.

In the chlorination of raw materials containing magnesium, calcium and manganese, the bottom zone accumulates, in addition to unchlorinated residue, a melt consisting chiefly of chlorides of the above elements, %: 66-68 CaCl<sub>2</sub>, 33-35 MgCl<sub>2</sub>, 1.5-2.0 FeCl<sub>2</sub>, 0.5-1.0 MnCl<sub>2</sub>.

The chloride melt is tapped at intervals through a hole in the lower part of the furnace. To keep it liquid, the bottom of the electric shaft furnace (ESF [shakhtnaya elektropech'; electric shaft furnace]) is warmed by current passed through a carbon (cryptolite) packing, to which it is supplied by two carbon electrodes. As chlorination advances, the height of the zone filled with unchlorinated furnace residue increases, with the result that the chlorination campaign must be broken off and the chlorinator shut down for cleaning. Depending on the conditions under which the equipment is operated, the campaign time for chlorination of titanium slags in an ESF varies from 1.5 to 6 months.

The chlorination zone, where the basic mass of the charge interacts with the chlorine, overlies the unchlorinated-residue zone. The temperature in this zone is raised to 1100°C by the heat released in the process. A further temperature rise cannot be permitted, since it results in rapid destruction of the lining and makes it difficult to condense the chlorination products. Thus, the temperature in this zone limits the productivity of the

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equipment. The height of this zone depends on the temperature, rate of chlorine supply, briquette dimensions, and the nature and particle dimensions of the concentrate and the carbon reducer. The height of the chlorination zone increases with increasing chlorine supply rate and briquette size. The chlorination zone is gradually displaced upward in the course of a campaign as the furnace residue accumulates. The rate of reaction-zone displacement determines the duration of the campaign. The high reaction-zone temperature and the bed of carbon-containing briquettes create conditions favoring the Boudouard reaction. Hence the exhaust gases of an ESF are characterized by a high CO/CO<sub>2</sub> concentration ratio (Table 27).

TABLE 27

Composition of ESF Exhaust Gases in Chlorination of Titanium Slags, %

| composition of gas | component contents during chlorination |   |
|--------------------|--|---|
|                    | by vaporized chlorine                  | by chlorine-air mixture containing ~70% Cl <sub>2</sub> |
| CO                 | 82-84                                  | 55-65   |
| CO <sub>2</sub>    | 11-12                                  | 5-10  |
| O <sub>2</sub>     | 0.3-0.4                                | 1-2   |
| HCl                | 6-traces                               | 6-traces  |
| COCl <sub>2</sub>  | 0.5-1                                  | 0.5-1   |
| N <sub>2</sub>     | rest                                   | rest  |

Because of the high carbon monoxide content in the exhaust gases, seepage of air into the condensation system must be excluded to prevent explosions.

To avoid possible explosions, the chlorinator and the upper-stage equipment of the condensation system are operated under a positive pressure. In addition, the chlorinator cover is provided with special blowout hatches as a safety measure against explosions.

Next above the chlorination zone is the zone in which the briquettes are heated. As they pass through this zone, the

briquettes are heated by exhaust gases to  $\sim 700^{\circ}\text{C}$ . Exchange reactions also take place in this zone between the titanium tetrachloride vapor and the readily chlorinated oxide components of the concentrate. The result is formation of chlorides of calcium, magnesium, iron, and other elements and secondary titanium dioxide, most of which is trapped in the briquette pores, from which the gas stream carries only insignificant amounts into the condensation system. Some condensation of the vapors of high-boiling chlorides ( $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , etc.), driven out of the reaction zone, also takes place on the cold briquettes in this zone. Hence the distribution of these chlorides between the chlorinator and the condensation system depends not only on the contents of the corresponding oxides in the raw material and the chlorination-zone temperature, but also on the height of the briquette-preheating zone. When a rich titanium slag with a small content of the oxides of these elements is chlorinated at high productivity with a thin blanket of briquettes, almost no melt is formed, since the corresponding chlorides are driven off into the condensation system. Toward the end of a campaign, the height of the preheating zone has been reduced to the minimum that supports operation without "blow-by" of unused chlorine into the condensation system.

The ESF chlorinator is fairly trouble-free in operation, chlorinates 96-97% of the titanium dioxide in the concentrate, and permits variation of productivity through a wide range. Its deficiencies include the intermittent nature of the process — the unchlorinated residue must be cleaned out at periodic intervals — low specific productivity on technical titanium tetrachloride [ $\sim 2$  tons/( $\text{m}^2 \cdot \text{day}$ )], and the complexity of preparing the raw material for chlorination (briquetting and coking the briquettes). The specific productivity of the ESF can be increased by stepped-up offtake of heat from the reaction zone, as by external cooling of the chlorinator. For this purpose, part of the shaft above the electrode zone is lined with lightweight firebrick. The chlorinator shell is protected from exposure to chlorine by two sheets of diabase tile 40 mm thick. During furnace operation, the outer surface of the shell is sometimes irrigated with water, so that

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substantially increased amounts of heats are taken out of the reaction zone and, consequently, the productivity of the equipment is raised. However, chlorides build up progressively on the surface of the diabase liner, with the result that the rate of heat transfer out of the chlorinator is lowered.

Concentrates that do not form a melt during chlorination can be processed in a shaft-furnace (SF [shakhtnaya pech'; shaft furnace]) chlorinator with mechanical residue unloading (Fig. 30). Use of this equipment permits a continuous chlorination process without shutdown of the chlorinator for cleaning and without expenditure of electric power to heat the chlorinator. In combination with the measure described above for stepping up heat offtake, these advantages of chlorination in the SF permit substantial increases in process productivity and improvement of industrial-hygiene conditions.

#### Technology of Chlorination in the Melt

Chlorination of powdered materials in a fused-chloride medium is a process that has been known since 1920 for magnesium oxide.

During the postwar period, one of the Soviet plants developed and introduced a method of chlorinating carnallite in the melt. In 1954, S.P. Solyakov proposed the use of fused chlorides as a medium for the chlorination of finely ground titanium slags. A schematic flow sheet of this process appears in Fig. 31. Used magnesium-bath electrolyte was used as the melt.

The process takes place as follows. Titanium slag, ground to  $-0.13+0.08$  mm, and  $-0.2+0.13$  mm petroleum coke are loaded into the

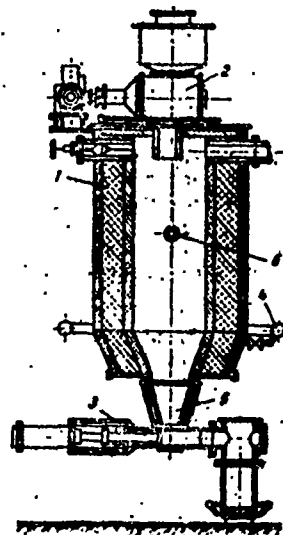


Figure 30. Diagram of shaft-furnace-type chlorinator with continuous unloading of chlorinated residue. 1) Furnace lining; 2) shaft-loading unit; 3) plunger-type unloader; 4) chlorine supply with tuyere; 5) water-cooled cone; 6) thermocouple.

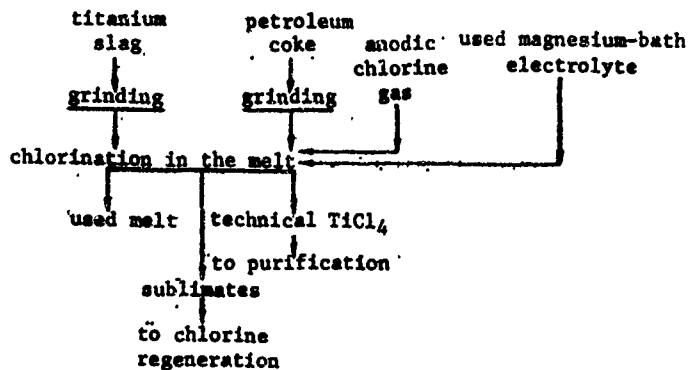


Figure 31. Flow chart of titanium tetrachloride production by chlorination of slags in the melt.

chlorinator by a worm feeder at the surface of a melt composed of high-boiling chlorides (Fig. 32). Chlorine is admitted at the bottom of the chlorinator. It is heated in the melt and reacts with the slag and coke. As it ascends through the melt, the flow of gases circulates it vigorously, preventing slag from settling onto the floor of the chlorinator and coke from floating to the surface. The gaseous chlorination products are piped from the top of the chlorinator into a condensation system. The nonvolatile chlorides and the unchlorinated residue that are formed are removed periodically as they accumulate, via the tap hole along with the melt. The chlorine-supply tuyere terminates in horizontal toothed chlorine distributors to provide more uniform distribution of the gas over the length of the chlorinator shaft. Some versions of the chlorinator have horizontal gratings made from high-alumina refractory in the shaft. The intended purpose of the distributor gratings is to further break down the gas bubbles and thereby increase the area of contact between the gas and liquid. However, laboratory tests conducted on a model chlorinator showed that these gratings are practically ineffective and even impede circulation of the melt and complicate the design of the chlorinator [39]. Overflow ducts, which serve to create directional circulation of the liquid, are built into the

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chlorinator wall opposite the chlorine distributor. In the absence of gas-distributor gratings, these overflow channels become unnecessary. The design of the chlorinator is substantially simplified as a result. Heat is taken from the melt through graphite rods around which it circulates; these rods contain pipes through which water is run to pick up the heat to be removed. Some of these rods are used as electrodes, which are switched in to warm the chlorinator.

The rate of the chlorination process in the melt depends on temperature, the degree to which the concentrate and coke are ground fine, the composition of the fused-salt bath, and the rate of chlorinating-agent supply.

There is a certain optimum size to which the concentrate and coke can be ground. Overgrinding of these materials does not increase chlorination rate. Normal operation of the chlorinator requires that the chlorine supply rate per unit sectional area of the chlorinator be no lower than a certain minimum that circulates the melt intensively enough to obtain uniform distribution of the concentrate and coke throughout its volume. In contrast to the ESF chlorinators, the exhaust gases are composed chiefly of  $\text{CO}_2$  in the case of fused-salt chlorination. As a rule, the carbon monoxide content does not exceed 5%. This fact, the cause of which has not definitely been established, increases the amount of heat liberated in chlorination and reduces the explosion hazard of the process.

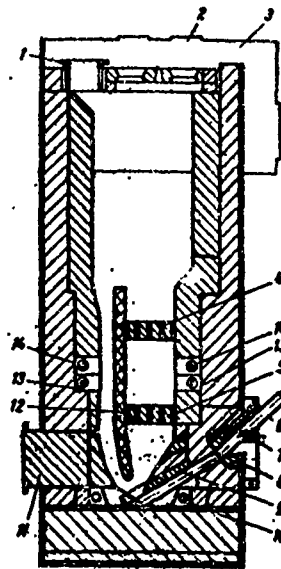


Figure 32. Diagram of chlorinator for chlorination in the melt. 1) Stack; 2) port and plug in roof; 3) roof; 4) upper chlorine-distributor grating; 5) lower chlorine-distributor grating; 6) chlorine supply pipe; 7) plug for cleaning; 8) chlorine-supply tuyere; 9) chlorine distributor; 10) lower electrode; 11) manhole; 12) overflow-duct wall; 13) electrode; 14) water-cooled rod.

Titanium slags are chlorinated at 750-800°C with continuous infeed of slag and coke.

The titanium dioxide concentration in the melt should be 0.5-1%, and that of carbon 7-9%. The height of the melt layer in the chlorinator is held in the range from 2.3 to 3.2 meters from the floor. Chlorine supply rate depends on chlorinator productivity and generally varies from 40 to 60 m<sup>3</sup> per hour per m<sup>3</sup> of melt.

In slag chlorination, the melt is partially replenished twice a day. Immediately after drainage of the melt, fresh used electrolyte taken from the magnesium baths is poured into the chlorinator to lower the concentrations of impurity chlorides and unreacted silica in the melt and bring the melt up to the proper level.

A single dose of spent electrolyte amounts to about 10-15% of the bath volume.

Melt and used-electrolyte compositions are listed below in %:

| KCl                             | NaCl | CaCl <sub>2</sub> | MgCl <sub>2</sub> | $\frac{FeCl_2 + MnCl_2}{+MgCl_2}$ | TiO <sub>2</sub> | C   | SiO <sub>2</sub> |
|---------------------------------|------|-------------------|-------------------|-----------------------------------|------------------|-----|------------------|
| Used magnesium-bath electrolyte |      |                   |                   |                                   |                  |     |                  |
| 75-80                           | 4-8  | 8-10              | 5-7               | 1-2                               | --               | --  | --               |
| Used chlorinator melt           |      |                   |                   |                                   |                  |     |                  |
| 30-40                           | 2-5  | 2-4               | 25-35             | 10-20                             | 0.5-1            | 7-9 | 6-3              |

The losses of titanium with the melt come to about 0.4-0.5%. The process of chlorination in the melt is continuous, briquetting and coking of the charge are unnecessary, and specific productivity is high (more than ten tons of titanium tetrachloride per day per square meter of chlorinator cross-sectional area). In many cases, it is possible to chlorinate at lower temperatures than in the case of the ESF because of the catalytic action of the salt-bath-melt components. Either chlorine or the chlorine-air mixture obtained during electrolysis of carnallite and magnesium chloride (recycling) may be used as the chlorinating agent.

A shortcoming of this process is the short service life of the chlorinator lining in melt chlorination as opposed to ESF

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chlorination. Melt chlorination cannot be used for titanium concentrates with high silica contents in the form of quartz, which, since it does not chlorinate as well as titanium dioxide, accumulates in the melt, increasing its viscosity and requiring frequent replenishment of the salt bath. In addition, the acid chlorides removed from the condensation-system units contain more titanium dioxide in melt chlorination than in ESP chlorination, especially when the chlorine-air mixture is used as the chlorinating agent. On the one hand, this results from venting of fine titanium dioxide and slag particles into the condensation system and, on the other, from the oxidation of titanium tetrachloride vapor by oxygen present in the chlorine-air mixture.

Footnotes

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|--------------------------------|--|--------------------------------|
| 174                            | <sup>1</sup> The chlorination process may also be inhibited by diffusion in the micropores of the briquette particles. For this reason, $k$ , $E_p$ , and $n$ may not characterize the true chemical reaction kinetics like the parameters $\lambda$ , $E$ , and $(n+1)/2$ . |                                |
| 176                            | <sup>2</sup> Aagard, L. and Cole, S. US Patent No. 2,622,005, 1952.  |                                |
| 176                            | <sup>3</sup> Bashour, J.T., Bikotsky, H.L. and Haimsohn, J.N. US Patent No. 2,974,009, 1964.   | 156<br>156                     |
| 178                            | <sup>4</sup> W.M. Weil, Norwegian Patent No. 98,243, 1961.   | 156                            |
| 178                            | <sup>5</sup> McKenna, British Patent No. 674,429, 1952.  | 169                            |
| 181                            | <sup>6</sup> N.L. Andersen, US Patent No. 2,842,425, 1958.   | 173<br>173                     |

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### Symbol List

| Manu-<br>script<br>page<br>No. | Russian | When<br>Typed | Meaning   |
|--------------------------------|---------|---------------|-----------|
| 156                            | тв      | с             | solid     |
| 156                            | газ     | газ           | gaseous   |
| 156                            | ж       | л             | liquid    |
| 169                            | г       | г             | gaseous   |
| 173                            | р       | р             | reaction  |
| 173                            | д       | д             | diffusion |

Chapter 10

SEPARATION OF CHLORINATION PRODUCTS AND  
PURIFICATION OF TITANIUM TETRACHLORIDE

Physicochemical Bases of Chloride Condensation and Purification  
of Titanium Tetrachloride

The behavior of the chlorination products during condensation is determined by their physicochemical properties, most important among which are vapor pressure, relative volatility, and melting point in the corresponding chloride systems. Below we present values of the boiling and melting points of certain chlorides that form along with titanium tetrachloride during slag chlorination, together with the solubilities of certain chlorides in  $TiCl_4$ .

|                     | $t_{boil}^{\circ}C$     | $t_{melt}^{\circ}C$    | solubility in<br>$TiCl_4$ , % |
|---------------------|-------------------------|------------------------|-------------------------------|
| $NaCl$ . . . . .    | 800                     | 1088                   | <0.01                         |
| $KCl$ . . . . .     | 775                     | 1407                   | <0.01                         |
| $CaCl_2$ . . . . .  | 782                     | 1900                   | $7.3 \cdot 10^{-5}$ (14°C)    |
| $MgCl_2$ . . . . .  | 714                     | 1413                   | <0.01                         |
| $MnCl_2$ . . . . .  | 650                     | 1150                   | $1.7 \cdot 10^{-5}$ (14°C)    |
| $FeCl_2$ . . . . .  | 647                     | 1026                   | <0.01                         |
| $FeCl_3$ . . . . .  | 303                     | 319                    | 0.005 (35°C)                  |
| $AlCl_3$ . . . . .  | 193 (under<br>pressure) | 180 (subli-<br>mation) | 0.15 (35°C)                   |
| $TiCl_4$ . . . . .  | -25                     | 136.5                  | .                             |
| $SiCl_4$ . . . . .  | -20                     | 57                     | .                             |
| $VOCl_3$ . . . . .  | -77                     | 127                    | .                             |
| $TiOCl_2$ . . . . . | -                       | -                      | 5.6 (130°C)                   |

\*Miscible in all proportions.

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The kinetics of condensation of the products of chlorination of titanium raw materials have not been studied. Accordingly, only thermodynamic relationships are used at present in computing the condensation yield of the chlorination products and their contents in the exhaust gases. The dimensions of the condensers, on the other hand, are determined by heat-transfer requirements and design considerations. This approach is quite justified if it is considered that the limiting stage of the process is not condensation proper, but offtake of the heat released in it. In other words, it is assumed that the speed with which equilibrium is established between the gas and the thin film of condensed phase that it washes is many times greater than the rate of heat transfer from this film to the coolant.

The amount of vapor leaving a condenser with the gas stream per unit of time is determined from the relation

$$M_1 n_{1 \text{ exh}} = \frac{M_1 p_{1 \text{ exh}} V_{\text{exh}}}{RT_{\text{exh}}}, \quad (82)$$

where  $M_1$  is the molecular weight of the vapor of the chloride being condensed,  $n_{1 \text{ exh}}$  is the number of gram-molecules of the substance being condensed that escape from the condenser per unit of time with the gas stream;  $p_{1 \text{ exh}}$  is the equilibrium partial pressure of this substance above the condensed phase at the exhaust-gas temperature;  $V_{\text{exh}}$  is the total volume of vapor-gas mixture leaving the apparatus per unit of time;  $T_{\text{exh}}$  is the exhaust-gas temperature.

The amount of vaporized matter at the entrance into the apparatus can be computed by the similar formula

$$M_1 n_{1 \text{ ent}} = \frac{M_1 p_{1 \text{ ent}} V_{\text{ent}}}{RT_{\text{ent}}}. \quad (83)$$

Here the letters "ex" denote the respective parameters at the entry into the apparatus. However, in contrast to the previous formula,  $p_{1 \text{ ent}}$  denotes in this case simply the partial pressure of the substance in the vapor-gas mixture at the entry into the apparatus.

The total pressure of the vapor-gas mixture in the apparatus equals the sum of the partial pressures of the gaseous products

that are not condensed under the particular conditions and the saturated vapors of the compounds that do condense:

$$\Sigma p_{i,2} = p_{tot,2} - \Sigma p_{i,2}^s \quad (84)$$

The over-all molar fraction of all gaseous products in the vapor-gas mixture leaving the condenser equals

$$Y_{tot,2} = \frac{\Sigma p_{i,2}}{p_{tot,2}} = 1 - \frac{\Sigma p_{i,2}^s}{p_{tot,2}} \quad (85)$$

Knowing the volume of the gases issuing from the apparatus per unit of time, we determine the corresponding volume of the vapor-gas mixture:

$$V_{2} = \frac{V_{tot,2}}{Y_{tot,2}} = \frac{V_{exh,2}^s \left( \frac{T_{2,2} \cdot 760}{273 p_{tot,2}} \right)}{1 - \frac{\Sigma p_{i,2}^s}{p_{tot,2}}} = V_{exh,2}^s \cdot \frac{T_{2,2} \cdot 760}{273 (p_{tot,2} - \Sigma p_{i,2}^s)} \quad (86)$$

where  $V_{exh,2}$  is the volume of gases leaving the apparatus per unit of time;  $V_{exh,2}^s$  is the volume of the same gases reduced to standard conditions.

Pressure is given in millimeters of mercury in Formula (86).

The value of  $V_{exh,2}^s$  is computed by adding the volumes of gaseous products that are formed, according to the equations of the chlorination reactions, on the basis of chlorinator productivity and the degree of chlorination for each component. If we know the composition of the chlorinating agent fed into the chlorinator and that of the exhaust gases, we can calculate the utilization of the chlorine, the total amount of air drawn into the condensing system and into the chlorinator through imperfect equipment seals (in operation under a partial vacuum), and the volume of gases leaving the condenser per unit of time. To derive the working formulas, we shall assume that the equipment is in steady-state operation. Let the chlorinating agent be a chlorine-air mixture in which the volumetric fraction of chlorine is  $c$ . We write the mass-balance equations with consideration of the fact that the outgoing vapor-gas mixture contains gases ( $N_2$ ,  $Cl_2$ ,  $O_2$ ,  $CO_2$ , and  $CO$ ). We denote the volumetric fractions of the

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above gases in the outgoing vapor-gas mixture by  $N_2$ ,  $Cl_2$ ,  $CO$ ,  $O_2$ , and  $CO_2$ , respectively; the total volume of air seepage will be denoted by  $A [m^3]$ , and the exhaust-gas volume by  $B [m^3]$ . All gas volumes will be assumed to have been reduced to standard conditions in this calculation. Since 2 moles of chlorine substitute 1 mole of oxygen in chlorination of any oxide component of the titanium concentrate, we calculate the amounts of oxygen and nitrogen introduced into the system and withdrawn from it. For convenience, the calculation will be made for  $100 m^3$  of chlorine-air mixture fed into the chlorinator.

1. Supplied to the system  $[m^3]$ :

a) with the chlorine-air mixture:

(86)

of oxygen and

$$100(1-c) \cdot 0,21$$

of nitrogen;

$$100(1-c) \cdot 0,79$$

b) with the aspirated air:

$$1.21A$$

of oxygen and

$$0.79A$$

of nitrogen;

c) with the chlorinated oxides

$$\frac{100c - BC_2}{2}$$

of oxygen.

2. Taken from the system with the vapor-gas mixture:

$$B(CO_2 + O_2 + \frac{1}{2} CO)$$

of oxygen and

$$B(1 - CO_2 - CO - O_2 - Cl_2)$$

of nitrogen.

Equating the amounts introduced to the amounts removed, we obtain a system of two equations in two unknowns (A and B):

$$\left. \begin{aligned} 100(1-c) \cdot 0,21 + 0,21A + \frac{100c - BC_2}{2} &= B(CO_2 + O_2 + \frac{1}{2} CO) \\ 100(1-c) \cdot 0,79 + 0,79A &= B(1 - CO_2 - CO - O_2 - Cl_2) \end{aligned} \right\}$$

Solving this system, we find

$$A = \frac{29c \cdot n + 21n - 79\pi(1-c)}{0.79m - 0.21n} \quad (87)$$

$$B = \frac{79(1-c)}{n} + \frac{29c + 21 - 79 \frac{m}{n}(1-c)}{0.79m - 0.21n} \cdot 0.79 \quad (88)$$

where  $n = i - \text{CO}_2 - \text{CO} - \text{O}_2 - \text{Cl}_2$ ;  $m = \text{CO}_2 + \text{O}_2 + \frac{1}{2} \text{CO} + \frac{1}{2} \text{Cl}_2$ .

For chlorination by vaporized chlorine,  $c = 1$  and the equations become somewhat simpler. Knowing the volume of the chlorinating agent introduced into the chlorinator per unit of time,  $V_{\text{chl}}^0$  [m<sup>3</sup>], we determine the volumes of aspirated air  $A^0$  and exhaust gases over the same time interval:

$$V_{\text{exh. gas}}^0 = B \cdot \frac{V_{\text{chl}}^0}{100}; \quad A^0 = A \cdot \frac{V_{\text{chl}}^0}{100} \quad (89)$$

The degree of chlorine utilization  $\alpha$  equals

$$\alpha = \frac{100c - 5\text{Cl}_2}{100c} = 1 - \frac{5\text{Cl}_2}{100c} \quad (90)$$

The formulas for calculation of A, B, and  $\alpha$  were derived by I.L. Paysakhov and used to analyze chlorinator performance.

The partial pressures of the saturated vapors can be found with the aid of experimental data on the equilibrium between the condensed phase and the vapor in the particular multicomponent system. Since such data are generally not available and even the equilibrium phase composition of the condensate is often unknown, it is assumed in engineering calculations that each chloride condenses in the form of an individual compound, forming a separate phase. In this case, the saturated-vapor partial pressure of the condensing compound equals the saturation vapor pressure above this compound at the same temperature. Since the corresponding data are available in the literature for the chlorides of all principal titanium-slag components, no particular difficulty is encountered in finding  $\Sigma p_{\text{par}}$ .

The quantities  $T_{\text{ent}}$  and  $T_{\text{exh}}$  are measured directly or specified in advance.

The  $p_{1 \text{ ent}}$  for the first condenser is determined from the composition of the vapor-gas mixture at the exit from the

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chlorinator:

$$(87) \quad p_{1ex} = p_{0ex} Y_{1ex} \quad (91)$$

(88) where  $Y_{1ent}$  is the molar fraction of the chloride in the vapor-gas mixture at the entry into the condenser.

The  $p_{1vkh}$  for subsequent condensers equal the  $p_{1ex}$  of the preceding condenser.

The amount of chloride trapped in the condenser per unit of time equals

$$M_1 (n_{1ex} - n_{1ent}) = M_1 \left( \frac{p_{1ex} V_{ex}}{RT_{ex}} - \frac{p_{1ent} V_{ent}}{RT_{ent}} \right) \quad (92)$$

The volume of vapor-gas mixture entering the condenser per unit of time is calculated by a formula analogous to (86):

$$(39) \quad V_{ex} = \frac{V_{ex,1at}^0 T_{ex} \cdot 760}{273 (p_{0ex} - \sum p_{ent,par})} \quad (93)$$

(90) where  $V_{ent,par}^0$  is the volume of gases, reduced to standard conditions, in the vapor-gas mixture leaving the condenser per unit time;  $\sum p_{ent,par}$  is the sum of the partial pressures of the chloride vapors at the entrance into the condenser.

The total pressure is practically the same in all units of the condensing system and equal to atmospheric.  $V_{vkh,gaz}^0$  and  $V_{ex,gaz}^0$  differ by the volume of air aspirated into the condenser under consideration. Disregarding this seepage and setting  $p_{tot} = 760$  mm, we obtain

$$M_1 (n_{1ex} - n_{1ent}) = \frac{n_{1ex}^0 V_{ex,1at}^0}{273R} \times \left( \frac{p_{1ex}}{1 - \frac{p_{1ex}}{760}} - \frac{p_{1ent}}{1 - \frac{p_{1ent}}{760}} \right) \quad (94)$$

The extent to which this chloride is trapped equals

$$\frac{n_{1ex} - n_{1ent}}{n_{1ex}} = 1 - \frac{p_{1ent}}{p_{1ex}} \left( \frac{1 - \frac{p_{1ex}}{760}}{1 - \frac{p_{1ent}}{760}} \right) \quad (95)$$

The total amount of chlorides condensed in the condenser per unit time equals

$$\sum M_i (n_{iex} - n_{ient}) \quad (96)$$

Distillation and rectification processes are important in the technology of purifying titanium tetrachloride. The basic characteristic needed for design of the equipment in which these processes take place is relative component volatility, by which we mean the ratio of the relative concentrations of these components in the equilibrium vapor and liquid phases. Thus, the relative volatility of components A and B is

$$\alpha_{AB} = \frac{Y_A}{Y_B} : \frac{X_A}{X_B} \quad (97)$$

where  $Y_A$  and  $Y_B$  are the concentrations of components A and B in the vapor phase, expressed in mole fractions;  $X_A$  and  $X_B$  are the concentrations of these components in the equilibrium liquid phase, expressed in mole fractions.

After clearing of suspended matter, technical titanium tetrachloride is a multicomponent system. The components present in it can be classified into three main groups:

- a) dissolved gases ( $\text{CO}_2$ ,  $\text{HCl}$ ,  $\text{Cl}_2$ ,  $\text{COCl}_2$ );
- b) liquids with moderate boiling points ( $\text{SiCl}_4$ ,  $\text{VOCl}_3$ ) and unlimited solubility in titanium tetrachloride;
- c) chlorides that are solid at room temperature ( $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{MgCl}_2$  and others) and dissolve poorly in titanium tetrachloride.

However, the total content of impurities dissolved in the  $\text{TiCl}_4$  represents only 0.5-1.0%. For this reason, and because of the fact that the impurity substances do not react chemically with one another, titanium tetrachloride is regarded as a binary system in the design of distillation apparatus. One component of this system is titanium tetrachloride and the other is the impurity to be removed. Consequently, the greatest interest attaches to the relative volatility of the impurity to be removed and titanium tetrachloride:

$$\alpha_{i/\text{TiCl}_4} = \frac{Y_i}{Y_{\text{TiCl}_4}} : \frac{X_i}{X_{\text{TiCl}_4}} \quad (98)$$

If the relative volatility exceeds unity, the vapor phase is richer in the impurity than the liquid at equilibrium with it.

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The reverse is the case if the relative volatility is smaller than unity. At  $\alpha = 1$ , the concentrations of titanium tetrachloride and the impurity are the same in the equilibrium liquid and vapor phases. In the first case, the impurity will concentrate in the distillate during rectification, and in the second it will collect in the column vat residue. In the third case, we deal with an azeotropic mixture that cannot be separated by rectification under the selected conditions. If experimental data are available on compositions of the equilibrium vapor and liquid phases, it is easy to determine the values of  $\alpha$  that correspond to various contents of the impurity in titanium tetrachloride. For ideal solutions ( $\text{TiCl}_4$ - $\text{SiCl}_4$ ,  $\text{TiCl}_4$ - $\text{VOCl}_3$  and others), relative volatility can be calculated for any composition from data on the vapor pressures above the pure impurity and  $\text{TiCl}_4$  at various temperatures. According to Raoult's law, to which ideal solutions are subject, the partial pressures of the components in the vapor phase at equilibrium with the liquid can be calculated by the equations

$$\begin{aligned} p_{\text{TiCl}_4} &= p_{\text{sat TiCl}_4} = p_{\text{TiCl}_4}^0 X_{\text{TiCl}_4} \\ p_1 &= p_{\text{sat } 1} Y_1 = p_1^0 X_1 \end{aligned} \quad (99)$$

where  $p_{\text{TiCl}_4}$  and  $p_1$  are the saturated-vapor partial pressures of the titanium tetrachloride and the impurity above the solution,  $p_{\text{tot}}$  is the total pressure in the system, and  $p_{\text{TiCl}_4}^0$  and  $p_1^0$  are the saturation vapor pressures above pure titanium tetrachloride and the impurity at the given temperature.

We obtain directly from these equations

$$\frac{Y_1}{Y_{\text{TiCl}_4}} = \frac{X_1}{X_{\text{TiCl}_4}} = \alpha_{1/\text{TiCl}_4} = \frac{p_1^0}{p_{\text{TiCl}_4}^0} \quad (100)$$

Thus, the relative volatility of the ideal-solution components equals the ratio of the saturation vapor pressures above these components at the given temperature. For a two-component system

$$X_1 + X_{\text{TiCl}_4} = 1$$

and

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$$p_{\text{total}} = p_{\text{TiCl}_4} + p_1 = p_1^0 X_1 + p_{\text{TiCl}_4}^0 (1 - X_1). \quad (101)$$

Solving this last equation for  $X_1$ , we find

$$X_1 = \frac{p_{\text{total}} - p_{\text{TiCl}_4}^0}{p_1^0 - p_{\text{TiCl}_4}^0}. \quad (102)$$

According to the Clapeyron-Clausius equation,

$$\ln \frac{p_1^0}{p_{\text{TiCl}_4}^0} = \frac{h_{\text{TiCl}_4}}{RT} \quad (103)$$

$$p_1^0 = p_1^s e^{-\frac{\lambda_1}{RT}} \quad (104)$$

where  $\lambda_{\text{TiCl}_4}$  and  $\lambda_1$  are constants having the sense of heats of formation of titanium tetrachloride and the impurity;  $h_{\text{TiCl}_4}$  and  $b_1$  are constants characteristic for these substances.

Consequently,

$$\frac{p_1}{p_{\text{TiCl}_4}} = \frac{p_1^0}{p_{\text{TiCl}_4}^0} = \frac{b_1}{h_{\text{TiCl}_4}} e^{\frac{\lambda_{\text{TiCl}_4} - \lambda_1}{RT}}. \quad (105)$$

Substituting the values of  $p_{\text{TiCl}_4}^0$  and  $p_1^0$  into the equation for  $X_1$ , we obtain finally

$$X_1 = \frac{p_{\text{total}} - \frac{b_1}{h_{\text{TiCl}_4}} e^{\frac{\lambda_{\text{TiCl}_4} - \lambda_1}{RT}}}{\frac{b_1}{h_{\text{TiCl}_4}} e^{-\frac{\lambda_1}{RT}} - \frac{b_1}{h_{\text{TiCl}_4}} e^{\frac{\lambda_{\text{TiCl}_4} - \lambda_1}{RT}}}. \quad (106)$$

This last equation can be used to compute the composition of a boiling ideal solution of the two components as a function of the total pressure and the boiling point if data are available on the saturation vapor pressures above the pure components at various temperatures.

Reference [27] considers the equilibrium distribution of an impurity with low solubility in titanium tetrachloride between the vapor and liquid phases. Such impurities include  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ , and the chlorides of alkali-, alkaline-earth-, and various other metals. Owing to the very low solubility in titanium tetrachloride, such a solution may be regarded as infinitely dilute even when it is saturated with the impurity. The vapor pressure of

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(101) the impurity above its infinitely dilute solution in titanium tetrachloride (the first phase) is calculated by Henry's law:

$$p_1 = KX_{1(I)} \quad (107)$$

(102) where K is Henry's constant for the particular component.

The symbol I indicates reference to the mole fraction of the impurity in the first phase. The vapor pressure of titanium tetrachloride above the first phase is subject to Raoult's law:

$$p_{\text{TiCl}_4} = p_{\text{TiCl}_4}^0 X_{\text{TiCl}_4(I)} = p_{\text{TiCl}_4}^0 (1 - X_{1(I)}) \quad (108)$$

(103) If there is a saturated solution of the impurity in the titanium tetrachloride, this solution should be at equilibrium with the second phase, which is the saturated solution of titanium tetrachloride in the impurity. Since the two solutions are at equilibrium, each component should have the same partial vapor pressure above them. If the solubility of titanium tetrachloride in the impurity is very low, its equilibrium partial pressure above the second phase is calculated from Raoult's law:

$$p_1 = p_1^0 X_{1(I)II} = p_1^0 (1 - X_{\text{TiCl}_4(II)}) \quad (109)$$

(105) where  $X_{1(n)II}$  and  $X_{\text{TiCl}_4(n)II}$  are the molar fractions of the impurity and the titanium tetrachloride, respectively, in the second phase, which is at equilibrium with the first.

(106) Equating the impurity partial pressures above the first and second phases, we find the value of Henry's constant in Eq. (107):

$$p_1^0 (1 - X_{\text{TiCl}_4(II)}) = KX_{1(I)}$$

$$K = \frac{p_1^0 (1 - X_{\text{TiCl}_4(II)})}{X_{1(I)}}$$
(110)

where  $X_{1(n)I}$  is the molar fraction of the impurity in the first phase, which is at equilibrium with the second phase.

Thus, Eq. (107) assumes the form

$$p_1 = \frac{p_1^0 (1 - X_{\text{TiCl}_4(II)}) X_{1(I)}}{X_{1(I)}} \quad (111)$$

If  $X_{\text{TiCl}_4(n)II} \approx 0$ , i.e., the solubility of titanium

tetrachloride in the impurity is negligibly low, we have

$$p_1 = \frac{p_1^0 X_{1(im)}}{X_{1(im)}}; \frac{p_1}{p_{tot}} = Y_1; \frac{p_{TiCl_4}}{p_{tot}} = 1 - Y_1;$$

and, consequently,

$$\frac{p_1}{p_{TiCl_4}} = \frac{Y_1}{1 - Y_1} = \frac{p_1^0 X_{1(im)}}{X_{1(im)} p_{TiCl_4}^0 (1 - X_{1(im)})}$$

whence

$$\frac{Y_1}{1 - Y_1} : \frac{X_{1(im)}}{1 - X_{1(im)}} = \alpha_{1/TiCl_4} = \frac{p_1^0}{p_{TiCl_4}^0 X_{1(im)}} = \frac{\alpha_{1/TiCl_4, id}}{X_{1(im)}} \quad (112)$$

where  $\alpha_{1/TiCl_4, id}$  is the relative volatility of the impurity and titanium tetrachloride calculated on the assumption that the solution of the impurity in the titanium tetrachloride is ideal:

$$p_1^0 / p_{TiCl_4}^0$$

If we consider the behavior of an impurity for which  $p_1^0 \ll \ll p_{TiCl_4}^0$ , its low solubility in titanium tetrachloride will make the solution boiling point practically equal to the boiling point of pure titanium tetrachloride. As a result,

$$\frac{p_1^0}{p_{TiCl_4}^0} = \text{const} \quad \text{and} \quad X_{1(im)} = \text{const.}$$

In this case, the relative volatility will be independent of impurity concentration in the titanium tetrachloride in the possible range of its variation, i.e.,

$$\alpha_{1/TiCl_4} = \text{const} (0 \leq X_{1(im)} \leq X_{1(im)}^*). \quad (113)$$

Since  $X_{1(im)} < 1$ ;  $\alpha_{1/TiCl_4} > \alpha_{1/TiCl_4, id}$ , i.e., the relative volatility of the low-solubility impurity is greater than that calculated by Raoult's law. Here, the lower the solubility of the impurity in titanium tetrachloride, the higher will be its relative volatility. A necessary condition for purification of the titanium tetrachloride of the impurity by rectification is that a differ from 1, which corresponds to the case

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$$X_{1(n)} \neq \frac{P_i}{P_{TiCl_4}} \quad (114)$$

If  $X_{1(n)} > \frac{P_i}{P_{TiCl_4}}$ , we have  $\alpha_{i/TiCl_4} < 1$ , and if  $X_{1(n)} < \frac{P_i}{P_{TiCl_4}}$ , we have  $\alpha_{i/TiCl_4} > 1$ .

In continuous-column rectification of a mixture for which  $\alpha_{i/TiCl_4} < 1$ , the vapor will be progressively impoverished in the impurity as it moves toward the column's refluxer. On the other hand, the reflux will become enriched in the impurity as it moves toward the evaporator. This enrichment of the reflux may continue until the impurity concentration in the liquid phase reaches  $X_{1(n)I}$ . When this concentration is reached, the impurity constitutes an independent phase and the mixture will behave as a heteroazeotrope, without further separation.

In continuous-column rectification of a mixture for which  $\alpha_{i/TiCl_4} > 1$ , the reflux will become impoverished in the dissolved impurity as it moves toward the evaporator. As they move toward the refluxer, on the other hand, the vapor will become richer in it, despite the fact that the vapor pressure above the pure impurity may be substantially lower than that above the pure titanium tetrachloride. The vapor will become richer in impurity

TABLE 28  
Solubility and Relative Volatility of Impurities Present in Titanium Tetrachloride

| basic component   | boiling point, °C | impurity          | boiling point, °C | solubility of impurity at boiling point of basic component, molar fraction | relative volatility of impurity and base |                         |                           |
|-------------------|-------------------|-------------------|-------------------|--|--|-------------------------|---------------------------|
|                   |                   |                   |                   |  | calculated from Raoult's law             | calculated by Eq. (112) | determined experimentally |
| TiCl <sub>4</sub> | 174               | Fe                | 21                | 0.0001   | 2.5 × 10 <sup>-3</sup>                   | 7.5 × 10 <sup>-2</sup>  | 7.5 × 10 <sup>-2</sup>    |
| TiCl <sub>4</sub> | 174               | Al                | 21                | 0.0001   | 0.7 × 10 <sup>-3</sup>                   | 2.3 × 10 <sup>-1</sup>  | —                         |
| TiCl <sub>4</sub> | 174               | AlCl <sub>3</sub> | 180               | 0.0001   | 9.1 × 10 <sup>-3</sup>                   | 1.3 × 10 <sup>-2</sup>  | 2.3 × 10 <sup>-2</sup>    |
| TiCl <sub>4</sub> | 174               | SnCl <sub>4</sub> | 221               | 0.0001   | 2.9 × 10 <sup>-3</sup>                   | 1.1 × 10 <sup>-1</sup>  | 0.22 × 10 <sup>-1</sup>   |

until the impurity concentration in the liquid phase reaches  $X_{1(n)I}$ . When this concentration is reached, the impurity will be an independent phase. There will be no further separation. The mixture will behave as a heteroazeotrope, and the impurity and the titanium tetrachloride will distill over in the proportions  $P_1^0 : P_{TiCl_4}^0$ .

If  $\alpha_{1/TiCl_4}$  is near unity, then even a minor change in the impurity's solubility in the titanium tetrachloride may have a substantial influence on the efficiency and direction of the separation process. A change in solubility can be brought about either by changing the solution boiling point by changing the pressure or by introducing a third component into the titanium tetrachloride. Table 28, which was borrowed from [27], may serve as an example of the relation between limited solubility and relative volatility.

As we see from the data in Table 28, the values found experimentally for the relative volatilities agree closely with those calculated by Eq. (112) despite the fact that the experimental value of  $c$  differs by several orders from that computed by Raoult's law.

#### Equilibria in Chloride Systems Encountered During Chlorination

According to V.A. Il'ichev and A.M. Vladimirova [7, page 148], the lower-limit freezing point of the  $CaCl_2$ - $MgCl_2$ - $MnCl_2$  system is about 590°C. In this system, the fusibility diagram is divided into two regions by a double-eutectic line that is nearly straight and passes through the 50%  $MgCl_2$ , 50%  $CaCl_2$  and 70%  $MnCl_2$ , 30%  $CaCl_2$  points. In the range of compositions around the figurative  $CaCl_2$  point, the primary crystallization product is calcium chloride. In the other region, a solid solution of magnesium and manganese chlorides is first to precipitate on crystallization. Sodium chloride additives lower the initial freezing points of melts of these chlorides quite substantially. Thus, for example, a  $CaCl_2$ - $MgCl_2$ - $MnCl_2$  melt with the components in 1:1:1 proportions begins to freeze at 613°C, while a melt containing 30% NaCl and 70% of the above mixture begins to solidify

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at 416°C. Addition of ferrous chloride to mixtures of calcium, magnesium, and manganese chlorides results in a sharp depression of the initial freezing point. Thus, for example, a melt containing 35% of a  $\text{CaCl}_2$ - $\text{MnCl}_2$ - $\text{MgCl}_2$  mixture taken in the proportions 3:6:1 and 65%  $\text{FeCl}_3$  has an initial freezing point of 222°C.

According to the same authors, the components of the ternary  $\text{MgCl}_2$ - $\text{FeCl}_2$ - $\text{MnCl}_2$  system form a continuous series of solid solutions. The lowest temperature at which crystallization begins in this system equals the melting point of magnesium chloride.

Binary and ternary systems of alkali-metal chlorides with iron and aluminum chlorides have been studied by numerous authors. According to Fischer and Simon [18], the compounds  $\text{NaAlCl}_4$  ( $t_{p1} = 151^\circ\text{C}$ ) and  $\text{KAlCl}_4$  ( $t_{p1} = 256^\circ\text{C}$ ) form in the  $\text{NaCl}$ - $\text{AlCl}_3$  and  $\text{KCl}$ - $\text{AlCl}_3$  systems. The eutectic between  $\text{NaCl}$  and  $\text{NaAlCl}_4$  contains 50.0-50.2% (molar) of  $\text{NaCl}$  and has a melting point of 150°C. The analogous eutectic between  $\text{KCl}$  and  $\text{KAlCl}_4$  melts at 250°C and contains 49% (molar) of  $\text{AlCl}_3$ . The pseudobinary system has a eutectic that melts at 125°C. The molar ratio of  $\text{NaCl}$  and  $\text{KCl}$  in this eutectic is 35:15. In the pseudobinary  $\text{NaCl}$ - $\text{KAlCl}_4$  system, the eutectic contains no more than 0.5% (molar) of  $\text{NaCl}$  and melts at 253°C. The ternary  $\text{NaCl}$ - $\text{NaAlCl}_4$ - $\text{KAlCl}_4$  eutectic melts at 123°C and has the following composition, in % (molar): 49-50  $\text{AlCl}_3$ ; 35  $\text{NaCl}$ ; 15  $\text{KCl}$ . It differs little in composition from the eutectic in the  $\text{NaAlCl}_4$ - $\text{KAlCl}_4$  pseudobinary system. Solid  $\text{NaAlCl}_4$  and  $\text{KAlCl}_4$  phases can coexist with  $\text{NaCl}$ . The same can be said of  $\text{NaCl}$ - $\text{KCl}$  and  $\text{KAlCl}_4$  solid solutions. However,  $\text{NaAlCl}_4$  and  $\text{KCl}$  react in accordance with the equation



The compounds  $\text{NaFeCl}_4$  and  $\text{KFeCl}_4$ , with melting points of 153 and 243°C, form in the  $\text{NaCl}$ - $\text{FeCl}_3$  and  $\text{KCl}$ - $\text{FeCl}_3$  systems. As in the case of aluminum chloride, the compound of ferric chloride with potassium chloride is more stable than its compound with sodium chloride. The difference between the standard heats of formation of the complexes of  $\text{FeCl}_3$  with  $\text{KCl}$  and  $\text{NaCl}$  at 25°C is 6.4 kcal. The binary eutectics of  $\text{NaFeCl}_4$  and  $\text{KFeCl}_4$  with  $\text{FeCl}_3$  and alkali-

metal chlorides contain 43 and 51% (molar) of NaCl and 45 and 52% (molar) of KCl [19]. In the binary  $\text{FeCl}_3\text{-AlCl}_3$  system, the components form a continuous solid-solution series [17]. The  $\text{NaCl-AlCl}_3\text{-FeCl}_3$  system has a ternary eutectic with a melting point of  $149^\circ\text{C}$  consisting of  $\text{NaCl}$ ,  $\text{NaAlCl}_4$ , and  $\text{NaFeCl}_4$  phases. The composition of this eutectic corresponds to 46% (molar) of  $\text{AlCl}_3$ , 3% (molar) of  $\text{FeCl}_3$ , and 51% (molar) of  $\text{NaCl}$  [20].

As substances of ionic structure, alkali- and alkaline-earth-metal chlorides are practically insoluble in titanium tetrachloride [21]. According to Moriyama and Inagaki [22], the solubilities of calcium chloride and manganese chloride in titanium tetrachloride at  $14^\circ\text{C}$  are  $7.3 \cdot 10^{-5}$  and  $1.7 \cdot 10^{-5}\%$ , respectively; magnesium chloride is practically insoluble below  $30^\circ\text{C}$ .

N.K. Druzhinina [7, page 225] found that the solubility of aluminum chloride in titanium tetrachloride increases sharply with temperature: it is 0.15% at  $55^\circ\text{C}$  and 7.15% at  $150^\circ\text{C}$ . In the presence of ferric chloride, the solubility of aluminum chloride is reduced by a factor of 1.5-2. The solubility of ferric chloride in titanium tetrachloride is much lower (0.05% at  $150^\circ\text{C}$ ). However, it is approximately 0.5% in the presence of aluminum chloride. Silicon tetrachloride, carbon tetrachloride, and vanadium oxytrichloride are miscible in all proportions with liquid titanium tetrachloride. The solubility of titanium oxychloride in titanium tetrachloride depends strongly on temperature. According to T.A. Zavaritskaya [7, page 195], the solubility of the oxychloride diminishes from 0.54 to 0.17% as the temperature is lowered from 26 to  $-20^\circ\text{C}$ . However, Ehrlich and Engel [23] reported that the solubility of  $\text{TiOCl}_2$  is 2.5% at  $25^\circ\text{C}$  and 5.6% at  $130^\circ\text{C}$ .

V.A. Il'ichev and K.D. Muzhzhavlev [24] studied the vapor pressure above certain melts in the  $\text{KCl-NaCl-MgCl}_2\text{-CaCl}_2$  system. At  $1000^\circ\text{C}$ , a melt containing 90%  $\text{MgCl}_2$ , 10%  $\text{KCl} + \text{NaCl}$  ( $\text{KCl}:\text{NaCl} = 2:1$ ) has a total vapor pressure of about 20 mm Hg. A melt containing 10%  $\text{MgCl}_2$ , 45%  $\text{KCl}$ , and 45%  $\text{NaCl}$  has a vapor pressure of 10 mm Hg at the same temperature. Addition of calcium chloride to this melt lowers its total vapor pressure considerably. Thus, for example, a melt containing 80%  $\text{CaCl}_2$ , 10%  $\text{MgCl}_2$ , and 10%

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KCl + NaCl (1:1) has a vapor pressure of 0.9 mm Hg at the same temperature. With rising temperature, vapor pressure drops off sharply. At 750°C above a melt containing 10% MgCl<sub>2</sub>, 45% NaCl, 45% KCl, the vapor pressure is 0.32 mm Hg, but 22.30 mm Hg at 1060°C. Analysis of melts containing MgCl<sub>2</sub>, NaCl, and CaCl<sub>2</sub> has shown that the magnesium and sodium chlorides are for the most part vaporized. The calcium chloride accumulates in the melt. The vapor pressures above alkali chloroaluminate melts are much lower than those above aluminum chloride. A diagram given by Dewing [25] indicates that the vapor pressure above NaAlCl<sub>4</sub> reaches one atmosphere at 867°C. Grothe [26] reports that the corresponding temperature for KAlCl<sub>4</sub> is 1017°C. According to V.G. Korshunov et al. [20], the complex compound NaFeCl<sub>4</sub> distills over without decomposing. The vapor pressure above fused NaFeCl<sub>4</sub> is subject to the equation  $\log p = -\frac{3600}{T} + 5.80$ . The vapor pressures of NaAlCl<sub>4</sub> and NaFeCl<sub>4</sub> are below 0.1 mm Hg above a mixture containing 5% (molar) of AlCl<sub>3</sub>, 5.4% (molar) of FeCl<sub>3</sub>, and 39.6% (molar) of NaCl at temperatures below 362°C. It is 1.2 mm at 477°C for NaAlCl<sub>4</sub> and 5.9 mm for NaFeCl<sub>4</sub>; at 590°C, it is 4.7 mm for NaAlCl<sub>4</sub> and 21.1 mm for NaFeCl<sub>4</sub>. Cook and Dunn [19] studied the interaction of FeCl<sub>3</sub> with sodium and potassium chlorides. At 1000°K, the equilibrium constant of the reaction  $KFeCl_{4(r-r)} = KCl_{r,r} + FeCl_{2(par)}$  is ~2.6, while the equilibrium constant of the dissociation reaction for the sodium ferrichloride is ~13. According to their data, the vapor pressures above these ferrichlorides are expressed by the equations

$$\log P_{NaFeCl_4} = 7.496 - \frac{3600}{T} \quad (350^\circ K < T < 1100^\circ K), \quad (116)$$

$$\log P_{KFeCl_4} = 5.657 - \frac{4517}{T} \quad (350^\circ K < T < 1100^\circ K). \quad (117)$$

According to N.K. Druzhinina [7, page 225], the vapor pressures of aluminum chloride and ferric chloride above their solutions in titanium tetrachloride are substantially higher than those calculated from Raoult's law. Ferric chloride sharply lowers the vapor pressure of aluminum chloride above the ternary mixture. At the same time, the partial pressure of the ferric chloride vapor rises in the presence of aluminum chloride.

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Equilibrium liquid-vapor diagrams for the  $TiCl_4-SiCl_4$ ,  $TiCl_4-CCl_4$ , and  $TiCl_4-CCl_3COCl$  systems [28, 29] indicate that these systems are practically ideal in the composition region neighboring on pure  $TiCl_4$ . The  $TiCl_4-CH_2ClCOCl$  system has an azeotrope containing 87% (molar) of  $CH_2ClCOCl$  with a boiling point of  $105^\circ C$  [29]. The  $TiCl_4-VOCl_3$  system is nearly ideal [30]. The volatility ratio  $VOCl_3/TiCl_4$  is 1.7 at small  $VOCl_3$  concentrations [7, page 195]. The vapor pressure of titanium oxychloride  $TiOCl_2$  above its solution in titanium tetrachloride at  $136^\circ C$  is very low, at 1 mm Hg at a 3%  $TiOCl_2$  concentration in the liquid [7, page 195]. The relative volatility of titanium tetrachloride and  $TiOCl_2$  is about 30.

#### Technology of Condensation of Chlorination Products

Condensing the chlorination products from the titanium raw material is an extremely complex matter for which no fully satisfactory industrial-scale equipment solution has been found. The complexity of the apparatus used for this conversion results from the sharp differences between the melting points of the chlorides that are formed. However, their boiling-point differences facilitate purification of the titanium tetrachloride during the condensation process. All presently known condensation methods except for that of so-called total condensation provide for collateral purification of the titanium tetrachloride of admixtures of less volatile chlorides that are solid at room temperature. This purification is done either by fractional condensation (the so-called combination and dry condensation systems) or as a result of chemical reaction of the iron, aluminum, and magnesium chlorides with alkali-metal chlorides. The various forms of condensation using the "salt" methods to purify the vapor-gas mixture fall into the latter category.

In the "total" condensation system, all chlorides leaving the chlorinator in the vapor state are condensed together as a result of irrigation of the vapor-gas mixture with cooled liquid technical titanium tetrachloride. The result is a pulp in which chlorides that are solid at room temperature are suspended in  $TiCl_4$ . As we noted above, this condensation system does not

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provide for separation of the chlorides in the condensation process. Hence all of the difficulties associated with the purification of titanium tetrachloride are postponed to later operations. Because of this deficiency, this condensation system has not yet come into industrial use for chlorination of multicomponent titanium raw materials.

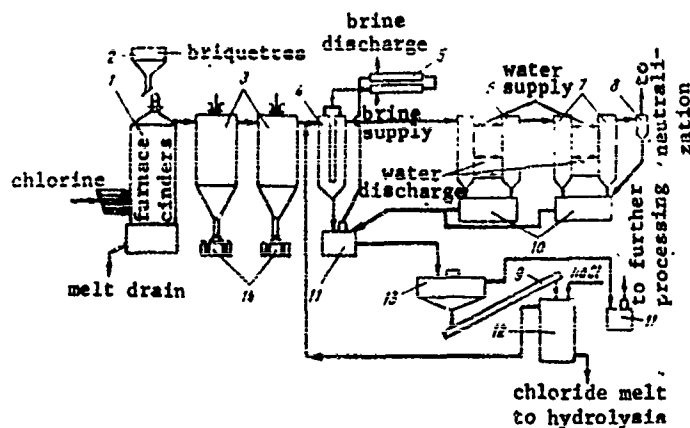


Figure 33. Diagram of combination condensation system. 1) Electric shaft furnace; 2) charging hopper; 3) hollow condenser; 4) sprinkler condenser; 5) circulating-pump condenser; 6) water-cooled condenser; 7) brine-cooled condenser; 8) trap; 9) slime worm conveyor; 10) titanium tetrachloride collector; 11) submersible-pump tank; 12) electric shaft furnace for pulp processing; 13) thickeners; 14) container.

Figure 33 presents a diagram of a combined-type condensation system. Vapor-gas mixture from the chlorinator first proceeds to a system consisting of two series-connected hollow condensers, which serve to cool the mixture and trap condensed chloride particles and dust (the so-called "sublimates"). The "sublimates" settle on the condenser walls, from which they trickle into buckets hung underneath the equipment, which are periodically emptied as the sublimates accumulate. "Sublimates" that are not trapped in the hollow condensers accompany the titanium tetrachloride vapors into the sprinkler condenser. Titanium- and silicon-tetrachloride vapors that are not trapped in the sprinkler

condenser are scavenged out in tubular condensers irrigated with brine at  $-10^{\circ}\text{C}$ . From this condenser, the gases pass through a trap, which collects chloride droplets, ore neutralized in a sanitary scrubber, and then released into the atmosphere. The temperature distribution of the vapor-gas mixture over the various units of equipment is as follows. At the entry into the first hollow condenser  $500-600^{\circ}\text{C}$ ; at the exit from the first condenser  $300-350^{\circ}\text{C}$ ; at the exit from the second condenser  $120-180^{\circ}\text{C}$ . Accordingly, the high-boiling magnesium, calcium, manganese, and ferrous chlorides are deposited for the most part in the first condenser. The second condenses ferric chloride and aluminum chloride. Since the initial condensation temperature of the vapors of these chlorides is below the melting points of their mixtures, the "sublimates" condense directly in the form of solid products, bypassing the liquid state. However, when titanium slags are chlorinated in a fused-salt medium with a high potassium chloride content, semifused and even liquid "sublimates" form in the hollow condensers. This phenomenon apparently results from volatilization of the complex compounds  $\text{KFeCl}_4$  and  $\text{KAlCl}_4$  from the salt melt; these readily fusible and comparatively nonvolatile substances condense in the liquid state in the hollow condensers.

A lining of these sublimates builds up on the condenser walls. This sublimate layer has low thermal conductivity. The result is lower operating efficiency of the hollow condensers [the average coefficient of heat transfer from the vapor-gas mixture to the outside air is  $2.5 \text{ kcal/m}^2/(\text{h.deg})$ ]. P.P. Khomyakov established the coefficient of thermal conductivity of the sublimates as a function of their temperature, bulk mass, and composition [40]. The walls of the hollow condenser are cleaned with scrapers carried by a rotating shaft that extends along the centerline of the apparatus. The scrapers are pressed against the buildup on the wall by their own weight, which is sufficient to remove the sublimates. For protection against exposure to chlorine, the top of the first condenser is lined internally with diabase tile or refractory concrete. The bottom of the first

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condenser and the second condenser are unlined. Here the buildup acts as a protective lining.

To increase the cooling area, the hollow condensers are sometimes replaced by clustered-pipe coolers, each with up to 14 0.5-m-diameter tubes.

The sprinkler condenser is a tube within a tube. The tubes are joined at the bottom by a common taper. The vapor-gas mixture first enters one tube, descends through it, and enters the other through the connecting taper. It then rises through this tube and is directed to the cooling condenser. Liquid titanium tetrachloride is used for cooling and condensation; it is fed continuously into the sprinkler condenser through nozzles at the top of each tube. These nozzles atomize the liquid titanium tetrachloride, setting up vigorous heat exchange between it and the vapor-gas mixture. The pulp formed in the sprinkler condenser drains through a special pipe in the connecting taper into the submersible-pump tank. The pump picks up the titanium tetrachloride from this tank, passes it through a cooled pipeline, and returns it to the nozzles. The excess titanium tetrachloride drains by gravity from the tank into a Dorr thickener. The upper discharge from the thickener, which is clarified titanium tetrachloride, goes for further purification. The residue of solid chlorides in titanium tetrachloride that drains out at the bottom of the thickener goes to an ESF [shakhtnaya elektropech'; electric shaft furnace] vaporizer in which the titanium tetrachloride is driven off. This furnace is also charged with sodium chloride. Heating at 500°C drives the titanium tetrachloride out of the solid chlorides, and it is sent for purification after condensation. The mixture of solid chlorides with sodium chloride forms a salt melt at 500°C. Here the iron and aluminum chlorides are bound into the less volatile sodium aluminochloride and ferrichloride and thus separated from the titanium tetrachloride. The fused chlorides from the ESF vaporizer are removed periodically through a tap hole and may be sent for reprocessing with the object of utilizing the chloride ion.

In the so-called "dry" condensation system, the position of the irrigating scrubber after the hollow condensers is taken by a bag filter. The function of this filter is to remove condensed dustlike solid chlorides from the titanium tetrachloride vapor, which then condenses either in a sprinkler condenser or tube coolers. The solid chlorides that settle on the bags are removed from them by shaking or by reverse flushing with process gases. For a bag filter to perform successfully, a stable temperature not much higher than the dew point of titanium tetrachloride must be maintained in it. Excessively high temperatures of the vapor-gas mixture in the bags increases the "penetration" of aluminum chloride vapor, which contaminates the titanium tetrachloride with solid admixtures. Moreover, raising the temperature above 180°C tends to rot the filter cloth. Lowering it below the dew point of titanium tetrachloride is inadmissible, since it causes titanium tetrachloride vapor to condense in the bag filter. As a result, the filter fabric becomes coated with a viscous film. Its resistance to passage of the gases rises and the process must be stopped because of excessive pressure in the condensation system. When a chlorine-air mixture containing 60% Cl<sub>2</sub> is used as a chlorinating agent, bag-filter temperatures are held at about 120°C. In chlorination with vaporized chlorine, the dew point of the titanium tetrachloride rises and the temperature in the filter must be increased accordingly.

After the filter, the gases have a dust content of 1.5-2 g/m<sup>3</sup>. The filter traps 40-50% of all sublimates. The remaining 50-60% are trapped in the hollow condensers. The filtration area per ton of titanium tetrachloride per day is about 6-7 m<sup>2</sup>.

As we noted above, the walls of the hollow condensers become coated during operation with a layer of sublimates that has low thermal conductivity. As a result, the condensation system of a high-output chlorinator occupies considerable plant floor space. By way of stepping up the cooling process for the vapor-gas mixture, it has been proposed that liquid titanium tetrachloride be injected into the vapor-gas mixture at the exit from the chlorinator. Process gases, i.e., gases tapped from the condensation

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system beyond the tubular cooler, may also be blown into the vapor-gas mixture for this purpose.<sup>(1)</sup> However, neither method is efficient enough, and both require dilution of the vapor-gas mixture. This makes subsequent condensation of the titanium tetrachloride vapor more difficult and increases the area occupied by the "tail-end" units of the condensation system.

The combined-type condensation system is extremely cumbersome, since it requires the use of numerous units for the tetrachloride-pulp processing stage. The "dry" system is somewhat more compact. However, substantial difficulties are encountered in attempts to build a workable bag filter. Glass cloth, which fails frequently, is used as the filtering material. Additional time is required for replacement of the bags.

There are several versions of the condensation system using chemical purification of the vapor-gas mixture to remove high-boiling chlorides. Purification is either by bubbling the vapor-gas mixture through fused  $\text{FeCl}_2$  and  $\text{AlCl}_3$  containing an excess of alkali-metal chloride<sup>(2)</sup> or by passing it through a packing composed of fragments of alkali-metal chlorides.<sup>(3)</sup> The iron and aluminum chlorides are then bound into less volatile and readily fusible complex compounds, which are thus separated from the titanium tetrachloride. The less volatile chlorides of calcium, magnesium, and manganese are also trapped by the resulting melt. Purified of solid impurities, the titanium tetrachloride vapor can be liquefied in cooling condensers. The bubbling process is less sensitive to clogging of the equipment by dusty impurities (carbon and oxide particles). However, the salt packing permits more thorough purification of the vapor-gas mixture and offers less resistance. In the salt-packing version, the temperature of the vapor-gas mixture at the entry into the salt bath must be held between 450 and 500°C, and the exit temperature between 150 and 200°C. In purification by bubbling through fused salts, the melt temperature is held at 200-250°C.

#### Purification Technology of Titanium Tetrachloride

The technical titanium tetrachloride arriving for purification contains about 1% suspended solid matter. Also present in Footnotes (1), (2), and (3) appear on page 217.

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it are small amounts of dissolved impurities: vanadium oxytri-  
chloride, aluminum chloride, ferric chloride, silicon tetrachloride,  
titanium oxychloride, elementary chlorine, phosgene, hexa-  
chlorobenzol, chloroacetyl chlorides, and a number of other im-  
purities. The following are concentration values for these im-  
purities converted to the elements or the corresponding compounds,  
in % (by mass): 0.03-0.1 V; 0.01-0.1 Al;  $\leq 0.02$  Fe; 0.01-0.3 Si;  
0.04-0.5  $TiOCl_2$ ; 0.03-0.15  $Cl_2$ ; 0.15  $COCl_2$ . To produce a high-  
quality metal, the titanium tetrachloride is subjected to a puri-  
fication process whose flow chart appears in Fig. 34.

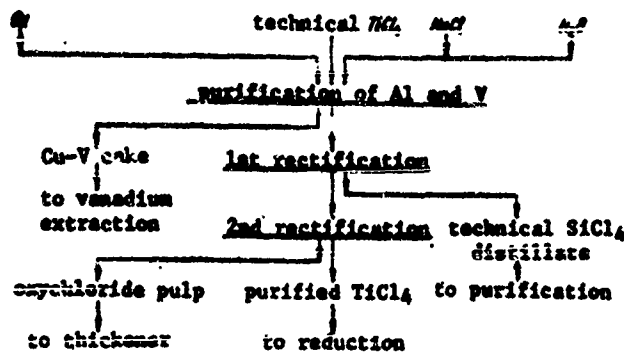


Figure 34. Flow chart of titanium tetrachloride purification.

The titanium tetrachloride is first purified of aluminum chloride and vanadium oxychloride. Both operations are performed in the same apparatus at room temperature. The aluminum is removed from the titanium tetrachloride by selective hydrolysis. For this purpose, the titanium tetrachloride is treated in a sealed reactor fitted with a stirrer with a small amount of moistened sodium chloride or carbon. The result is that the aluminum chloride forms aluminum oxychloride, which is practically insoluble in titanium tetrachloride. The amount of moisture introduced must be slightly greater than stoichiometric:

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A large moisture excess is detrimental, since it results in additional titanium losses through formation of the metal's oxychloride:



Removal of aluminum from  $\text{TiCl}_4$  with moistened carbon always involves contamination of the  $\text{TiCl}_4$  by oxygen, and this is a major deficiency of this purification method.

After purification of aluminum, the titanium tetrachloride is purified of vanadium oxychloride. Selective reduction of the vanadium oxychloride by powdered copper is used for this purpose. The amount of copper powder used is about 0.3% of the mass of the technical titanium tetrachloride. Since the vanadium oxychloride concentration is low and titanium tetrachloride reacts vigorously with copper powder, it must be assumed that the direct reducing agent in this process is not the copper itself, but the complex salt of titanium trichloride with cuprous chloride. The copper-vanadium cake formed as a result of purification contains up to 5% vanadium and can be used as a raw material for the preparation of pure vanadium reagents. The cake is cementable. Thus the purified titanium tetrachloride is removed from the apparatus with continuous agitation and filtered through glass cloth.

After filtering, the titanium tetrachloride contains <0.01% of aluminum and vanadium. It then goes for purification of silicon tetrachloride and most of the dissolved gases. These compounds are removed by rectification.

Steel columns with slotted grid plates are normally used for rectification. The plate slot width is 3 mm and the open slot area represents 17-19% of plate area. The distance between plates is 250-350 mm. The total number of plates ranges from 30 to 40. At a column diameter of 600 mm and a reflux ratio of 3-4 in the distillation section, column productivity is 2.5 tons/h of purified titanium tetrachloride.

The purified tetrachloride is withdrawn at the bottom of the column, while the silicon tetrachloride is removed from the reflux section in the form of a distillate. The dissolved gases are withdrawn from the refluxer through a hydroseal filled with distillate, which serves to prevent entry of atmospheric moisture into the rectification column. The purified titanium tetrachloride contains <0.01% Si. The silicon tetrachloride usually contains 20-50% of  $TiCl_4$ .

The last operation is to purify the titanium tetrachloride of the titanium oxychloride and other products of incomplete chloride hydrolysis. This is done by rectification in grid-plate or packed columns. The less volatile products of incomplete hydrolysis are accumulated in the vat of the column, from which they are periodically pumped as a pulp with titanium tetrachloride, filtered, and dumped.

After passage through all purification stages, the titanium tetrachloride is taken off in the form of a distillate containing about 0.004% V; 0.006% Si; 0.004% Fe; 0.004% Al, and 0.001-0.002% O.

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Footnotes

| Manu-<br>script<br>Page<br>No. |   |
|--------------------------------|---|
| 213                            | <sup>1</sup> Säurefabrik Schweizerhall. British patent No. 716,681, 1954.                     |
| 213                            | <sup>2</sup> Consolidierte Alkaliwerke. German patent No. 628,953, 1936.                      |
| 213                            | <sup>3</sup> G.V. Seryakov and A.P. Masterova. Author's certificate (USSR) No. 116,207, 1958. |

Symbol List

| Manu-<br>script<br>Page<br>No. | Russian | When<br>Typed | Meaning          |                |
|--------------------------------|---------|---------------|------------------|----------------|
|                                |         |               |                  | 1.             |
|                                |         |               |                  | Vol. 37,       |
|                                |         |               |                  | 2.             |
|                                |         |               |                  | 257, pag       |
| 192                            | пл      | m             | melting          | 3.             |
| 192                            | кип     | b             | boiling          | 4.             |
| 193                            | отх     | exh           | exhaust          | page 267       |
| 193                            | вх      | ent           | entry            | 5.             |
| 194                            | газ     | gas           | gaseous          | 1948, Vo       |
| 194                            | обш     | tot           | total            | 6.             |
| 194                            | пар     | par           | vapor            | Tetrachl       |
| 196                            | хл      | chl           | chlorinator      | of Liter       |
| 201                            | н       | n             | [not identified] | 7.             |
| 202                            | ид      | id            | ideal            | tanium a       |
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|                                |         |               |                  | 8.             |
|                                |         |               |                  | Vol. 25,       |
|                                |         |               |                  | 9.             |
|                                |         |               |                  | 247, pag       |
|                                |         |               |                  | 10.            |
|                                |         |               |                  | <u>Khimi</u> ( |
|                                |         |               |                  | 11.            |
|                                |         |               |                  | 1939, Vo       |
|                                |         |               |                  | 12.            |
|                                |         |               |                  | 13.            |
|                                |         |               |                  | Vol. 17,       |
|                                |         |               |                  | 14.            |
|                                |         |               |                  | page 112       |

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Part IV

METALLOTHERMIC REDUCTION OF TITANIUM COMPOUNDS

Chapter 11

GENERAL INFORMATION ON THE PROCESS AND THE  
PROPERTIES OF TITANIUM, SODIUM,  
MAGNESIUM, AND THEIR COMPOUNDS

The reduction of titanium tetrachloride by magnesium or sodium and the reduction of titanium oxides by calcium (calcium hydride) and aluminum are the processes of greatest theoretical and practical interest.

The industrial production of titanium is presently based on the reduction of titanium tetrachloride by magnesium (magnesiothermic method) or sodium (sodiothermic method).

In the former case, the reduction products — titanium sponge, magnesium, and magnesium chloride — are usually separated by distilling the magnesium and magnesium chloride out of the titanium sponge at about 1000°C with reactor residual pressures varying from a few millimeters of mercury at the beginning of the process to a few microns at the end of the process (in the so-called vacuum-separation process).

In the latter case, the reduction products — titanium sponge, sodium chloride, and a small amount of unreacted sodium — are separated by leaching the reaction mass obtained after reduction with a dilute hydrochloric acid solution (the so-called hydro-metallurgical method).

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A titanium sponge with a low oxygen content cannot be obtained by reduction of titanium oxides with aluminum and calcium (calcium hydride) because of the inadequate affinity of these reducing agents to oxygen and the high solubility of aluminum and calcium in the reduced titanium. Further, the acquisition of titanium sponge of adequate purity with respect to other admixtures (other than oxygen) requires the use of titanium oxides of higher purity than the titanium tetrachloride normally used for this purpose. At the present time, there are no industrial processes for the production of titanium oxides of purity approaching that of the titanium tetrachloride used to obtain the metal.

It appears that as such methods are developed in the future, the production of extremely pure titanium oxides will cost more than that of titanium tetrachloride of the same purity. Thus the aluminum and calcium reduction of titanium oxides that have not been specially purified may be useful for the production of non-structural titanium, titanium-based master alloys, and materials suitable for subsequent purification of oxygen, as by electrolytic refinement.

Reduction of sodium and potassium fluotitanates is also applicable to a very limited degree, chiefly because of the high cost of these compounds and the complexity of separating the reduction products and regenerating the fluorine.

The high chemical activity of titanium at elevated temperatures and the technological difficulties that attend the reduction of titanium compounds made it impossible until comparatively recently to obtain sufficiently reliable data on the thermodynamic properties of this metal and its chemical compounds.

Only after improvement of the magnesio- and sodiothermic methods of reducing titanium and development of the iodide method did it become possible to obtain adequate amounts of relatively pure metal.

Thus, in evaluating the highly contradictory data from various authors on the thermodynamic properties of titanium and its compounds, it is necessary to give special attention to the method

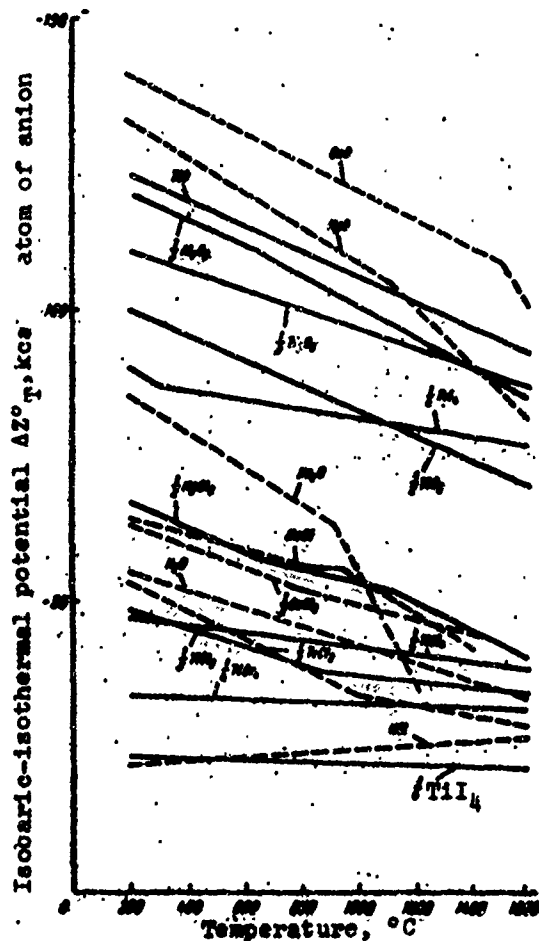


Figure 35. Isobaric-isothermal potentials of formation of titanium, magnesium, sodium, and calcium compounds.

used to prepare the specimens of titanium and its compounds, their chemical purity, and the methods that the authors used to obtain the thermodynamic characteristics.

Systematized data on the thermodynamic properties of titanium and its compounds are given in [1-6, 12 and 13].

Table 29 gives the values that appear to be most reliable at the present time for the thermodynamic properties of titanium and

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some of its compounds. These data will be used below in the thermodynamic calculations pertaining to the thermal metallurgy of titanium.

To permit evaluation of the affinity of titanium to oxygen, nitrogen, carbon, and the halogens, Fig. 35 shows temperature curves of the isobaric-isothermal potentials of the compounds, which have a bearing on processes for the metallothermic reduction of titanium. The isobaric-isothermal potentials were calculated by the method originally proposed by M.I. Temkin and L.A. Shvartsman [15].

The method has been modified to some degree for calculation of the quantities in which we are interested. The calculation was carried out by the equations

$$\Delta Z_T^0 = \Delta H_{T_0}^0 - T \Delta S_{T_0}^0 - M_0 \Delta a - M_1 \Delta b - M_2 \Delta c - M_{-2} \Delta e \pm \Delta H_{T_0}^0 \mp \frac{\Delta H_{T_0}^0}{T_0} \cdot T, \quad (1)$$

where  $\Delta a$ ,  $\Delta b$ ,  $\Delta c$ , and  $\Delta e$  are the slopes of the temperature-curve equations of heat capacity for the substances participating in the reaction;  $M_0$ ,  $M_1$ ,  $M_2$ , and  $M_{-2}$  are the temperature coefficients whose values are given in Fig. 36, and  $T_p$  is the phase-transformation temperature.

Equation (1) and the values of the coefficients  $M_0$ ,  $M_1$ ,  $M_2$ , and  $M_{-2}$  are valid for calculation of the isobaric-isothermal potentials of all chemical reactions.

We see from Fig. 35 that the oxides, chlorides, and fluorides of titanium, including its lower chlorides, have high chemical stability in the temperature range from 200 to 1600°C, with the result that the strongest reducing agents, such as calcium, sodium, magnesium, etc., must be used to reduce them.

An exception is titanium monochloride (TiCl), whose enthalpy of formation under standard conditions is plus 122 kcal/mole, a figure that indicates its low-temperature instability [4, 10]. At temperatures above 800°C, titanium monochloride is detected spectrally in the gaseous phase [4, 8, 20, 28-30].

TABLE  
 Thermodynamic Properties of Titanium, Magnesium, Sodium, and

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 Some of

| Metal and compound                   | $\Delta_f H_{298}^\circ$<br>kcal/mole | $\Delta_f S_{298}^\circ$<br>kcal/(deg.mole) | $C_p$ kcal/(deg.mole) |              |              |                 |
|--------------------------------------|---------------------------------------|---|-----------------------|--------------|--------------|-----------------|
|                                      |                                       |   | $\cdot$               | $\cdot 10^2$ | $\cdot 10^3$ | $\cdot 10^{-4}$ |
| Ti <sub>2</sub>                      | —                                     | 7.3 ± 0.05 [2]                              | 5.9                   | 2.00         | —            | — [2]           |
| TiO <sub>2</sub> (rutile)            | 219 ± 1.5 [3]                         | 12.0 ± 0.05 [3]                             | 17.21                 | 1.08         | —            | -3.59 [3]       |
| TiO <sub>2</sub> (anat.)             | 375.5 ± 9.0 [3]                       | 18.83 ± 0.2 [3]                             | 7.31                  | 53.52        | —            | — [3]           |
| TiO                                  | 185.0 ± 10 [3]                        | 8.3 ± 0.1 [3]                               | 10.57                 | 3.6          | —            | -1.28 [3]       |
| TiCl <sub>4</sub> (liquid)           | 191.6 ± 0.2 [1,5]                     | 56.6 ± 0.4 [1]                              | 24.61                 | 1.54         | —            | -1.84 [2]       |
| TiCl <sub>3</sub> (s)                | 172.2 ± 0.4 [6]                       | 32.2 ± 0.1 [6]                              | 22.99                 | 3.92         | —            | -0.12 [7]       |
| TiCl <sub>3</sub> (l)                | 122.7 ± 0.7 [1]                       | 24.1 ± 1.0 [1]                              | 17.00                 | 2.76         | —            | -0.26 [3]       |
| TiF <sub>4</sub> (s)                 | 392.5 ± 0.4 [1]                       | 24.2 [1]                                    | 24.61 <sup>a</sup>    | 1.54         | —            | -3.24 [3]       |
| K <sub>2</sub> TiF <sub>6</sub> (s)  | —                                     | —   | —                     | —            | —            | —               |
| K <sub>2</sub> TiCl <sub>6</sub> (s) | 16.8 [1]                              | 87.8 [1]                                    | —                     | —            | —            | —               |
| Ti <sub>2</sub> U <sub>3</sub> (s)   | 99.2 ± 2.0 [1]                        | 64.8 [1]                                    | 24.61 <sup>a</sup>    | 1.54         | —            | -1.94 [3]       |
| TiBr <sub>4</sub> (s)                | 148 ± 0.5 [1]                         | 57.2 ± 4.0 [3]                              | 24.61 <sup>a</sup>    | 1.54         | —            | -1.94 [3]       |
| Mg                                   | —                                     | 7.77 ± 0.1 [3]                              | 8.23                  | 2.45         | —            | -0.103 [3]      |
| MgCl <sub>2</sub> (s)                | 153.2 ± 0.2 [3]                       | 21.4 ± 0.2 [3]                              | 18.9                  | 1.48         | —            | -2.08 [3]       |
| MgCl <sub>2</sub> (l)                | 68.8                                  | 1.99  | 16.08                 | 2.88         | —            | —               |
| Na                                   | —                                     | 12.8  | 8.24                  | 2.35         | —            | —               |
| NaCl (s)                             | 98.7 [3]                              | 17.4  | 14.88                 | 3.51         | —            | —               |
| TiN                                  | 50.4 ± 0.5 [1]                        | 7.24  | 11.91                 | 0.94         | —            | -2.96 [3]       |
| TiC                                  | 42.89 ± 0.6 [3]                       | 11.9  | 11.83                 | 0.88         | —            | -2.52 [3]       |

- \*<sup>1</sup>Temperature and heat of sublimation.
- \*<sup>2</sup>Assumed to be the same as for TiCl<sub>4</sub>.
- \*<sup>3</sup>According to [11], in the range from 380-800° C  $\Delta_f H_{298}^\circ = 34772 + 238.05 T - 139.63 T \log T - 0.0047 T^2$ .
- \*<sup>4</sup>According to [1], at 400° C  $\Delta_f H_{298}^\circ = 22600 - 28.97 T$ .

The value given in Table 29 for the enthalpy of formation of magnesium monochloride MgCl was calculated by the thermochemical rule of logarithms as the mean between the enthalpies for formation of NaCl and AlCl<sub>3</sub>; the entropy of MgCl was calculated after V.M. Latimer [10]; the specific heat of MgCl was assumed to be the same as that of NaCl. Thermodynamic data for MgCl are given by Kelley [31] and Sandler [32].

As we see from Fig. 35, titanium has the strongest affinity to chlorine, fluorine, and oxygen in the compounds TiCl<sub>4</sub>, TiF<sub>4</sub>, and TiO. The very high affinity of titanium to oxygen in the

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29  
Some of their Compounds Under Standard Conditions

| Melting point (°C) | Heat of fusion, kcal/mole | Boiling point, °C    | Heat of evaporation, kcal/mole | Temperature of phase transformation, °C | Heat of phase transformation, kcal/mole |
|--------------------|---------------------------|----------------------|--------------------------------|---|---|
| 1650 [2]           | 4.5±0.5 [2]               | 3200 [2]             | 102.5                          | 862 [2]                                 | 0.35 [2]                                |
| 1850 [3]           | 15.5±2.5 [3]              | 3000 [3]             | —                              | —                                       | —                                       |
| 2120 [3]           | —                         | —                    | —                              | 200 [3]                                 | 0.22 [3]                                |
| 2020 [3]           | 14.0 [3]                  | —                    | —                              | 901 [3]                                 | 0.82 [3]                                |
| —26 [1]            | 2.24 [1]                  | 130.5 [1]            | 8.65 [1]                       | —                                       | —                                       |
| 905 [1]            | —                         | 800 <sup>a</sup> [1] | 36.8 <sup>a</sup> [1]          | —                                       | —                                       |
| 1027 [1,5]         | 8.75 [1]                  | 1600 [1]             | 80.3 [1]                       | —                                       | —                                       |
| —                  | —                         | 283 <sup>a</sup> [1] | 21.8 <sup>a</sup> [1]          | —                                       | —                                       |
| 180 [1]            | 4.0 [1]                   | 370 [1]              | 14.05 [1]                      | —                                       | 21.6(sub.)                              |
| 30 [1]             | 2.19 [1]                  | 220 [1]              | 10.6 [1]                       | —                                       | 16.7(sub.)                              |
| 649.5 [3]          | 2.0±0.1 [3]               | 1105 [3]             | 32.0 [3]                       | —                                       | —                                       |
| 714 [3]            | 10.3±0.3 [3]              | 1418 [3]             | 32.7±2.0 [3]                   | —                                       | —                                       |
| —                  | —                         | —                    | —                              | —                                       | —                                       |
| 97.8               | 0.83                      | 888                  | 22.4±0.6                       | —                                       | —                                       |
| 800.5 [3]          | 7.4 [3]                   | 1485 [3]             | 48.7 [3]                       | —                                       | —                                       |
| 3150 [1]           | 20.0 [1]                  | —                    | —                              | —                                       | —                                       |
| 2800 [1]           | 20.0 [1]                  | —                    | —                              | —                                       | —                                       |

monoxide, which is formed on reduction of higher oxides of titanium, results in incomplete reduction of these oxides even when a strong reducer such as calcium is used. The situation is further aggravated by the fact that the monoxide formed at elevated temperatures as a result of reduction of higher titanium oxides dissolves in titanium.

For similar reasons, the oxygen content in the titanium cannot be lowered beyond 1.5-2.0% in the reduction of titanium oxides by magnesium [17].

On the other hand, the presence of small quantities of oxygen and especially of nitrogen in titanium are sharply detrimental to its mechanical properties.

Titanium absorbs hydrogen actively and forms solid solutions and hydrides with it. The solubility of hydrogen in titanium (with solid-solution formation) is about 1.0%; the hydrides TiH and TiH<sub>2</sub> form with 1.7-2.3% of hydrogen in titanium [17, 18]. In

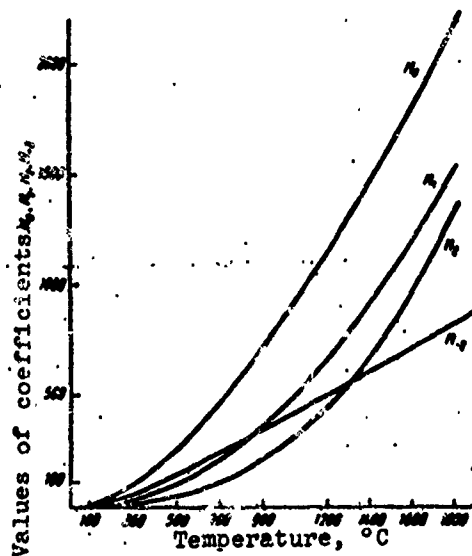


Figure 36. Values of the coefficients  $M_0$ ,  $M_1$ ,  $M_2$ , and  $M_3$  at various temperatures.

contrast to oxygen and nitrogen, almost all of the hydrogen absorbed by titanium can be removed from the metal at 1000-1200°C and a residual pressure of  $1 \cdot 10^{-3}$  mm Hg.

Titanium reacts with carbon, CO, CO<sub>2</sub>, and other carbon compounds at elevated temperatures, a result of which in the extreme case is the formation of stable, high-melting titanium carbides. Up to 0.5%, carbon dissolves in titanium forming a solid solution.

At elevated temperatures, titanium reacts and forms alloys with iron, aluminum, silicon, nickel, chromium, and manganese; there are a number of intermetallic compounds of titanium with these metals [17, 18].

Thus, we see that contact of titanium with these materials must be avoided in the reduction process, since they will otherwise contaminate the metal. Hence the high-temperature reduction process may not be carried out in equipment lined with materials that contain oxides, carbon, nitrogen, etc. Only beryllium and

Hydrogen ab-  
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TABLE 30  
Vapor Pressures of Metals and Chemical Compounds, atm

| Element of compound | Temperature, °C       |                       |                       |                        |     |      |                       |
|---------------------|-----------------------|-----------------------|-----------------------|------------------------|-----|------|-----------------------|
|                     | 77                    | 83                    | 108                   | 117                    | 124 | 132  | 337                   |
| Ti                  | 5.69·10 <sup>-3</sup> | 5.27·10 <sup>-3</sup> | 1.86·10 <sup>-1</sup> | 9.23·10 <sup>-15</sup> | 1.0 | 1.43 | 4.79·10 <sup>-7</sup> |
| TiCl <sub>4</sub>   | 1.47·10 <sup>-3</sup> | 1.10·10 <sup>-3</sup> | 3.65·10 <sup>-1</sup> | 7.79·10 <sup>-14</sup> | 1.0 | 1.43 | 1.58·10 <sup>-7</sup> |
| TiCl <sub>3</sub>   | 1.10·10 <sup>-3</sup> | 1.10·10 <sup>-3</sup> | 1.00·10 <sup>-1</sup> | 3.21·10 <sup>-14</sup> | 1.0 | 1.43 | 1.31·10 <sup>-7</sup> |
| TiCl <sub>2</sub>   | 2.64·10 <sup>-3</sup> | 1.10·10 <sup>-3</sup> | 1.00·10 <sup>-1</sup> | 1.41·10 <sup>-14</sup> | 1.0 | 1.43 | 1.73·10 <sup>-7</sup> |
| Ni                  | 1.10·10 <sup>-3</sup> | 1.10·10 <sup>-3</sup> | 1.00·10 <sup>-1</sup> | 3.04·10 <sup>-14</sup> | 1.0 | 1.43 | 5.04·10 <sup>-8</sup> |
| NiCl <sub>2</sub>   | 1.10·10 <sup>-3</sup> | 1.10·10 <sup>-3</sup> | 1.00·10 <sup>-1</sup> | 1.5·10 <sup>-14</sup>  | 1.0 | 1.43 | 1.78·10 <sup>-7</sup> |
| NiCl <sub>3</sub>   | 2.64·10 <sup>-3</sup> | 1.10·10 <sup>-3</sup> | 1.00·10 <sup>-1</sup> | 3.04·10 <sup>-14</sup> | 1.0 | 1.43 | 3.97·10 <sup>-7</sup> |
| NiCl <sub>4</sub>   | 1.10·10 <sup>-3</sup> | 1.10·10 <sup>-3</sup> | 1.00·10 <sup>-1</sup> | 3.04·10 <sup>-14</sup> | 1.0 | 1.43 | 3.76·10 <sup>-7</sup> |
| TiCl <sub>3</sub>   | 2.64·10 <sup>-3</sup> | 1.10·10 <sup>-3</sup> | 1.00·10 <sup>-1</sup> | 3.04·10 <sup>-14</sup> | 1.0 | 1.43 | 3.76·10 <sup>-7</sup> |
| TiCl <sub>2</sub>   | 1.10·10 <sup>-3</sup> | 1.10·10 <sup>-3</sup> | 1.00·10 <sup>-1</sup> | 3.04·10 <sup>-14</sup> | 1.0 | 1.43 | 3.76·10 <sup>-7</sup> |

| Element of compound | Temperature, °C       |                        |                        |                        |                        |                        |                        |
|---------------------|-----------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
|                     | 277                   | 287                    | 327                    | 367                    | 407                    | 447                    | 507                    |
| Ti                  | 6.41·10 <sup>-6</sup> | 1.00·10 <sup>-10</sup> | 1.00·10 <sup>-10</sup> | 1.00·10 <sup>-10</sup> | 1.00·10 <sup>-10</sup> | 1.00·10 <sup>-10</sup> | 1.00·10 <sup>-10</sup> |
| TiCl <sub>4</sub>   | 1.41·10 <sup>-3</sup> | 1.41·10 <sup>-3</sup>  | 1.41·10 <sup>-3</sup>  | 1.41·10 <sup>-3</sup>  | 1.41·10 <sup>-3</sup>  | 1.41·10 <sup>-3</sup>  | 1.41·10 <sup>-3</sup>  |
| TiCl <sub>3</sub>   | 4.08·10 <sup>-3</sup> | 4.08·10 <sup>-3</sup>  | 4.08·10 <sup>-3</sup>  | 4.08·10 <sup>-3</sup>  | 4.08·10 <sup>-3</sup>  | 4.08·10 <sup>-3</sup>  | 4.08·10 <sup>-3</sup>  |
| TiCl <sub>2</sub>   | 1.00·10 <sup>-3</sup> | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  |
| Ni                  | 1.00·10 <sup>-3</sup> | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  |
| NiCl <sub>2</sub>   | 1.00·10 <sup>-3</sup> | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  |
| NiCl <sub>3</sub>   | 1.00·10 <sup>-3</sup> | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  |
| TiCl <sub>3</sub>   | 1.00·10 <sup>-3</sup> | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  |
| TiCl <sub>2</sub>   | 1.00·10 <sup>-3</sup> | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  | 1.00·10 <sup>-3</sup>  |

thorium oxides have adequate stability with respect to titanium at elevated temperatures.

The weaker -- by comparison with calcium, sodium, and magnesium -- affinity of titanium to chlorine at the temperatures that are of practical interest for the reduction process, the ready availability of titanium tetrachloride, its adequate purity and relatively low cost, and the possibility of producing high-grade titanium from it make  $TiCl_4$  the basic raw material at the present time for the metallothermic reduction of titanium.

A factor of prime importance in this process is that the titanium tetrachloride can be reduced to the metal by such common and relatively cheap reducing metals as magnesium and sodium. These metals are practically insoluble in titanium [17, 18], so that the titanium is more completely reduced and easier to separate from these metals on completion of the process; nor is separation of the magnesium or sodium chlorides formed in the process from the reduced titanium a matter of any great complexity.

Table 20 lists vapor pressures of metals and compounds that participate in titanium metallothermic reduction processes, according to Kelley and Man [13]. The vapor pressures of the lower titanium chlorides were also determined in [3, 5, 14, 23, 25-27].

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Symbols

| Manu-<br>script<br>Page<br>No. | Russian | When<br>Typed | Meaning |
|--------------------------------|---------|---------------|---------|
| 228                            | тв      | s             | solid   |
| 228                            | рутил   | rutil         | rutile  |
| 228                            | жидк    | l             | liquid  |
| 228                            | ф       | f             | phase   |

## Chapter 12

### REDUCTION OF TITANIUM OXIDES

#### Reduction of Titanium Dioxide by Calcium

Processes in which the oxides are reduced by aluminum and silicon are now in extensive use for the production of various metals and alloys. Alumino- and silicothermy are used on a particularly broad scale to produce ferroalloys, aluminum, magnesium, and other nonferrous and rare metals; such reducing agents as magnesium, sodium, calcium, and others are also widely used.

As we saw from Fig. 36, calcium has the strongest affinity to oxygen among these metals. This makes it the most suitable reducing agent for production of titanium from its oxides.

The first attempt to reduce titanium dioxide with calcium was made in 1904 by Khupert [transliterated from Russian], and another in 1907 by Burger. Later, in 1923, Ruff and Brintzinger succeeded in reducing titanium dioxide to 88% by this method [40]. The reduction of  $TiO_2$  by calcium in a steel bomb in the presence of  $CaCl_2$  was studied by Mardek [2].

By reducing  $TiO_2$  with calcium in a fused mixture consisting of 75%  $CaCl_2$  and 25%  $BaCl_2$  at  $750^\circ C$  in an argon atmosphere, Kroll obtained a product that was found to contain 98% metallic titanium. This metal showed good hot ductility, but was cold-short because of its content of unreduced titanium monoxide.

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Kubaschewski and Dench report that when  $TiO_2$  is reduced by calcium at  $1000^\circ C$ , a metal containing no more than 0.1%  $O_2$  can be produced [43]. According to other investigators,  $TiO_2$  cannot be reduced to the metal even at  $1200^\circ C$  in the presence of a substantial calcium excess, owing to the formation of titanium monoxide, which has a strong affinity to oxygen [44].

G.A. Meyerson et al. reduced  $TiO_2$  with calcium in a mixture with  $CaCl_2$  and  $BaCl_2$  taken in 3:1 proportions [45]. The reaction was conducted at about  $1000^\circ C$  in a steel bomb with an argon atmosphere and a 50% calcium excess. The resulting product was leached in 10% hydrochloric acid solution and then contained 90-98% Ti with a yield of 75-80% of theory. This material was also reduced by calcium in the presence of  $CaCl_2$  and  $BaCl_2$ , with the result that the metal's purity was raised to 97.2-99.5%, although the useful yield was only 67%.

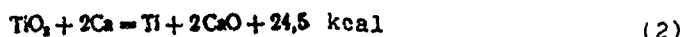
Later studies of the calcium reduction of  $TiO_2$  produced better results. It was shown that metal containing less than 0.07%  $O_2$  and having a terminal elongation of up to 30% could be produced by an improved calciothermic process [17].

Because of its strong affinity to nitrogen ( $\Delta Z_{1000^\circ C}^\circ = -20$  kcal/g-atom), calcium absorbs it actively on exposure to air. Metallic titanium has an even stronger affinity to nitrogen than does calcium ( $\Delta Z_{12730^\circ C}^\circ = -51$  kcal/g-atom). When titanium oxides are reduced with calcium, therefore, practically all of the nitrogen present in the calcium goes over into the titanium, to the sharp detriment of its quality.

As a rule, specially purified vacuum-distilled calcium contains from 0.05 to 0.15%  $N_2$ . Thus, the nitrogen content in the resulting titanium is also increased by 0.05-0.15%.

Despite the high cost of distillation-purified calcium and the difficulties noted above in connection with the use of calcium to reduce  $TiO_2$ , it is reported that calciothermic reduction of titanium oxides is in use in Canada on an industrial scale [17, 47]. Without elaborating, Kroll affirms that continuous titanium reduction is easily based on the calciothermic process [52].

The reduction of  $TiO_2$  by calcium proceeds in accordance with the exothermic reaction



This reaction is usually conducted at  $1000^\circ C$ . Then, as we see from Fig. 36, the affinity of calcium for oxygen is about 120 kcal/g-atom, while the affinity of titanium to oxygen in the most stable oxide  $TiO$  is 15 kcal/g-atom lower at the same temperature. This indicates the thermodynamic possibility of complete calcium reduction of  $TiO$ .

However, it must be remembered here that the values given for the free energy of  $TiO$  apply for the case in which the titanium monoxide is in the free state. On the other hand, the titanium monoxide formed in the calcium reduction of  $TiO$ , a process run at about  $1000^\circ C$ , forms a solid solution with metallic titanium. At a  $TiO$  content of about 0.2% in the solid solution and temperatures from 1000 to  $1200^\circ C$ , the thermodynamic potential of formation of the  $Ti-O$  bond becomes practically equal to that for  $CaO$ , with the result that it is theoretically impossible to reduce  $TiO_2$  to an oxygen content of less than 0.05-0.07% in the titanium [17, 69]. Kelley and Man present the following data on the equilibrium oxygen content in titanium for calciothermic reduction of titanium oxides: 0.01% at  $627^\circ C$ , 0.02% at  $727^\circ C$ , 0.03% at  $927^\circ C$ , 0.05% at  $1127^\circ C$ , and 0.10% at  $1273^\circ C$  [87].

An excess of calcium (25-50%) over theory is usually used to reduce  $TiO_2$  to the metal. The reaction goes practically to completion at  $1000-1100^\circ C$ , temperatures at which there is good contact between the calcium and the reducing-oxide particles as a result of the high fluidity of calcium at  $1000-1100^\circ C$  and its appreciable vapor pressure ( $p_{1000^\circ C} = 11 \text{ mm Hg}$ ).

At temperatures above  $1300^\circ C$ , the calciothermic reduction of  $TiO_2$  is complicated by the formation of calcium titanate, which cannot be removed effectively from the resulting reaction mixture by acid leaching [47].

The calcium oxide formed in the reduction process is an obstacle to the formation of large titanium particles, so that a

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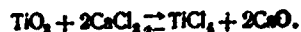
which accounts  
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To prevent  
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metal powder with particle sizes of a few microns is obtained. On subsequent leaching of the reaction mass, this powder oxidizes readily and is contaminated, so that high-grade metal cannot be obtained.

(2) Calcium chloride or a eutectic mixture of calcium chloride with barium chloride, which melts at 600°C, is added to the initial charge as a flux to produce coarser powder. At 1000°C, the solubility of CaO in CaCl<sub>2</sub> and in the CaCl<sub>2</sub>-BaCl<sub>2</sub> eutectic mixture is about 25%. Usually, calcium chloride is introduced in the proportions necessary to convert all of the CaO that is formed into the compound 2CaO·CaCl<sub>2</sub>. When the CaO dissolves in the flux added to the reactor, the high-melting CaO phase vanishes, and this helps aggregate the reduced titanium into particles up to 100 μm in size. Another effect of adding CaCl<sub>2</sub>, apart from dissolving the CaO, consists in the fact that only 20% of the calcium and a certain quantity of TiO<sub>2</sub> are dissolved in the fused CaCl<sub>2</sub> at 1000°C, so that TiCl<sub>4</sub> forms in the melt by the reaction



Despite the fact that the equilibrium TiCl<sub>4</sub> concentration in the melt is insignificant owing to the presence of dissolved calcium in it, the reaction



which accelerates reduction, proceeds continuously and favors more complete reduction of the titanium and formation of coarse particles of the reduced metal.

To prevent oxidation and nitriding of the calcium and titanium, the calcium reduction of TiO<sub>2</sub> is usually conducted in a sealed reactor made from heat-resistant steel. Argon is fed into the reactor after loading the briquetted charge and evacuating the air. To prevent sublimation of the calcium out of the reaction zone, the reactor is enclosed in a special sealed furnace and an excess argon pressure is created in it.

When the reaction is complete, the reactor is held at 1000-1100°C for about 1 hour to complete the reduction of the oxides;

the reactor is then extracted from the furnace and the reaction mass unloaded after cooling. The reaction mass is ground and treated with a large excess of cold water to prevent overheating of the material during hydrolysis of the  $\text{CaCl}_2$ , since this would result in sharply lowered quality of the titanium as a consequence of its high-temperature oxidation. The water-leached reaction mass is washed with dilute hydrochloric acid until all of the calcium chloride, calcium hydroxide, and excess metallic calcium have been dissolved.

When dilute hydrochloric acid is used, some of the titanium is lost with the solution. Nitric, acetic, formic, and other acids may be used instead of hydrochloric. Dilute nitric acid, which has a passivating effect on the surface of titanium, dissolves much less of it than does hydrochloric.

The washed metallic powder is again washed with alcohol and dried in a vacuum at 40-50°C. When the powder obtained has a grain size of about 100  $\mu\text{m}$  and the reaction mass is carefully treated, it is possible to produce titanium of 99-99.5% purity, with the remainder chiefly nitrogen, oxygen, iron, etc. With very careful processing and two-stage reduction, as we indicated above [43], it is sometimes possible to obtain titanium with an  $\text{O}_2$  content of about 0.1%.

However, the calciothermic method can hardly be expected to produce a metal containing 0.1%  $\text{O}_2$  or less in the production of titanium on an industrial scale.

Calcium hydride may be used instead of calcium to lower the temperature of the titanium-oxide reduction and improve the quality of the titanium.

The calcium hydride method of reduction has been elaborated by G.A. Meyerson et al. [50, 51], Alexander [53], Khoks [transliterated from Russian],<sup>1</sup> and others. This method was used extensively in Germany during the Second World War in the preparation of thermite mixtures [49, 54].

Calcium hydride is usually obtained by treating calcium with dry, purified hydrogen at 400-600°C. The resulting product is

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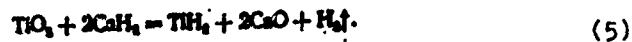
easily ground into a powder. On interaction with atmospheric moisture, calcium hydride decomposes readily -- especially in the powdered form -- by the reaction



For this reason, measures that prevent the hydride from coming into contact with the air must be taken in preparing the charge of calcium hydride with the oxide to be reduced; it is also necessary to use  $\text{CaH}_2$  in the form of small fragments rather than a powder.

Calcium hydride decomposes into its component elements at temperatures above  $800^\circ\text{C}$ . The equilibrium hydrogen pressure above calcium hydride at  $970^\circ\text{C}$  is 760 mm Hg.

The net reaction in which  $\text{TiO}_2$  is reduced by calcium hydride is expressed by the equation



It was assumed that as a highly active reducing agent, the atomic hydrogen liberated on the decomposition of calcium hydride in the reduction of  $\text{TiO}_2$  reduced the  $\text{TiO}_2$  to the metal, and that the calcium functioned only to bind the oxygen [12]. However, G.A. Meyerson et al. established that the principal reducing reagent here is not the hydrogen, but the calcium, which is liquid and to some extent gaseous at the reaction temperature. The reducing capacity of calcium in this case is greater than that of atomic hydrogen [6, page 195; 51].

As a rule, the titanium hydride produced by the calcium hydride method consists of particles finer ( $3\text{-}5\ \mu\text{m}$ ) than the titanium particles obtained by calciothermic reduction of  $\text{TiO}_2$  in the presence of  $\text{CaCl}_2$ . However, owing to the substantially higher corrosion resistance of titanium hydride as compared with fine titanium powder, it is oxidized and nitrified to a much lesser degree than titanium powder during the subsequent leaching of the mixture. As a rule, the washed and dried titanium hydride powder is 99.5% pure (with the remainder for the most part oxygen in the form of oxide films). The reaction mixture is leached out and washed in the same way as in the calciothermic method.

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The titanium hydride produced in this way is pressed into briquettes and sintered at about 600°C in a vacuum. During sintering, the oxide films are partially reduced by atomic hydrogen liberated as a result of dissociation of the titanium hydride. The sintered metal contains substantially smaller amounts of oxygen and hydrogen as compared with the initial TiH<sub>2</sub>.

The calcium hydride process is conducted at 800-1000°C in equipment made from heat-resistant steel and similar in design to the equipment used for the calciothermic process. After evacuation, the reactor is filled with thoroughly purified and dried hydrogen, which forms the atmosphere for the reduction process and cooling of the reaction products in the reactor.

Powdered titanium hydride may be used to make billets of compact malleable metal or, in the electrovacuum industry, as a source of extremely pure hydrogen, which is needed to fill certain components. A method for reduction of TiO<sub>2</sub> by a mixture of calcium and sodium hydrides in a melt consisting of NaCl and CaCl<sub>2</sub> has been patented in the USA [13]. The sodium and calcium hydride are prepared at 800°C by hydrogenation of the slurry produced by electrolyzing a mixture of CaCl<sub>2</sub> and NaCl and containing more than 20% of metallic calcium. The TiO<sub>2</sub> reduction reaction is conducted in a hydrogen atmosphere at 1000°C; argon is fed into the reactor at the last stage of the process to terminate the reaction. The reaction products are cooled in the argon atmosphere, washed with alcohol and dilute acid, and then dried. Titanium of about 95% purity can be obtained by this method.

#### Reduction of Titanium Dioxide by Magnesium and Other Reducing Agents

The calciothermic and calcium-hydride methods examined above are predicated on the use of expensive reducing agents, to the great detriment of economy in the production of titanium. For this reason, many attempts have been made to use more readily available reducing agents to reduce TiO<sub>2</sub>.

One of the most active and relatively cheap reducing agents is metallic magnesium.

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However, the affinity of magnesium to oxygen in the temperature range of practical interest (800-1000°C) is so little stronger than that of titanium for oxygen in the monoxide that it is impossible to reduce  $TiO_2$  to the metal with magnesium. Research done by various authors [51]<sup>2</sup> indicates that a product containing only about 92-95% Ti is obtained when  $TiO_2$  is reduced by magnesium, and that the rest is basically lower titanium oxides. Thus, reduction of a material containing 96.5%  $TiO_2$  with magnesium containing 0.02%  $N_2$  at a temperature of 1000°C and an Mg:  $TiO_2$  ratio of 3:1 in the presence of  $CaCl_2$  and  $BaCl_2$  yields a product containing 93-93.2% Ti, 2.5-2.7%  $O_2$ , 0.54% Mg, 0.01%  $N_2$ , and other impurities [56].

Winkler and Schneider established that TiO is formed preferentially on reduction of  $TiO_2$  with magnesium [44]. Kubaschewski and Dench obtained titanium containing ~2.5%  $O_2$  by this method [43]. In Kroll's opinion, magnesium is unsuitable for reduction of  $TiO_2$  because of the impossibility of removing the  $TiO_2$  and MgO completely from the reaction mass [59].

Research was done in 1956 on the reduction of titanium dioxide by magnesium and calcium in two stages [60]. The best results were obtained under the following conditions: reduction of  $TiO_2$  with magnesium at 1000°C, leaching of the product with 5% hydrochloric acid, vacuum distillation of the magnesium at 1250-1450°C, reduction of the reaction mass with calcium at 1000°C, leaching with 5% hydrochloric acid, degasification of the product at 840°C. The resulting metal contained 0.16-0.2%  $O_2$ , 0.01-0.03% Mg, and 0.05-0.07% Ca. The metal was cold-short.

Certain investigators have attempted to reduce  $TiO_2$  with sodium and with an alloy of sodium with calcium [28, 29]. It was established that metallic sodium reduces  $TiO_2$  only to the lower titanium oxides at 900-950°C. Better results were obtained in reducing  $TiO_2$  with an alloy of 60-70% Na and 40-30% Ca at temperatures above 700°C. In this case, however, the final titanium contained up to 5% of impurities.

Attempts have also been made to reduce titanium dioxide with hydrogen [62-64, 65]. However, it was again impossible to produce

metallic titanium by this method because titanium has a much stronger affinity to oxygen than does hydrogen. Wyse established that hydrogen reduces titanium only to a compound with the chemical formula  $Ti_3O_5$  at  $900^\circ C$  [62]. V.A. Reznichenko and F.B. Khalimov, who reduced titanium dioxide with a steam-and-hydrogen mixture containing 0.02% Ca, 0.12% Fe, 0.04% Mg and other impurities, established that  $TiO_2$  is reduced to  $Ti_3O_5$  by hydrogen at  $1050^\circ C$ , while a mixture of  $Ti_2O_3$  and  $Ti_3O_5$  is obtained above  $1050^\circ C$  [65, page 11].

Repeated attempts to reduce titanium dioxide with carbon were equally unsuccessful. On reducing  $TiO_2$  with carbon in an arc furnace, Moisson obtained a product containing 5% C. The carbon content in the titanium could be reduced to 2% by two reheatings of the product with a  $TiO_2$  additive [66]. Reduction of  $TiO_2$  by carbon in a vacuum furnace at temperatures above  $2400^\circ C$  produced a material containing no less than 4.6% C in the form of titanium carbide [67].

Junker showed that when a mixture of carbon and titanium dioxide reacts in a vacuum at  $800-1200^\circ C$ , i.e., under conditions such that the CO and  $CO_2$  are removed rapidly enough from the reaction zone, the product consists of titanium carbide and lower titanium oxides [68]. Here the course of the reactions leading to metallic titanium is complicated by the metal's high capacity to dissolve the carbides and lower titanium oxides that are formed.

Wasch and Dawihl proposed a method in which  $TiO_2$  is reduced by carbon in an inert-gas atmosphere or vacuum in an arc furnace.<sup>3</sup> Steinberg and Wiener reduced  $TiO_2$  with lampblack in a vacuum at  $1100-1200^\circ C$  with 0.5-1.0 mole of carbon per mole of  $TiO_2$ . The  $Ti_2O_3$  obtained as a result of the reaction was mixed in equimolecular quantities with carbon and heated in a vacuum to  $1500-1800^\circ C$ . It was possible to reduce the  $Ti_2O_3$  only to  $TiO$ .

#### Reduction of Titanium Dioxide by Aluminum

Thermodynamically, aluminum is capable of reducing titanium dioxide at temperatures below  $1400^\circ C$  only to the monoxide  $TiO$ , whose free energy of formation is 5-10 kcal/g-atom of oxygen

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higher than that of  $Al_2O_3$ . At the same time, we know that aluminum fuses with titanium to form a continuous series of solid solutions and intermetallic compounds [39]. This has a strong influence on the course of the reduction process and promotes the reaction



The aluminothermic method eliminates the use of expensive equipment, inert gases, etc., since it is an out-of-furnace metallurgical process and hence much simpler and cheaper.

An ingot of tough alloy that is easily separated from the slag is formed in the aluminothermic reaction, and for this reason the reaction mixture does not require use of chemical or other separation methods. This also makes the process simpler and less expensive.

A shortcoming of aluminothermic reduction is that the titanium is not a pure product, but an alloy with aluminum that is contaminated by oxygen. The very fact that the titanium is obtained in the form of the Ti-Al alloy is not decisive, since the overwhelming majority of structural alloys based on titanium contain aluminum (up to 20%). What is important is that the Ti-Al alloy is rather heavily contaminated by oxygen because the reaction takes place in a charge that is exposed to atmospheric air.

N.N. Murach et al. [76] were the first to produce alloys of titanium with aluminum by an open metallothermic process. The titanium contents in the alloys that they obtained varied from 25 to 75%.

One report describes use of the aluminothermic method to produce a Ti-Al alloy containing 69% Ti, 11% Al, 7%  $O_2$ , remainder iron, silicon, and insoluble residues. This alloy was named "altam" [71]. The literature gives no details of the Altam process. It has been reported [80] that  $TiO_2$  can be reduced by the aluminothermic method to obtain a Ti-Al alloy containing 0.02%  $O_2$ , a statement which we find difficult to credit.

Certain theoretical problems in connection with aluminothermic reduction of  $TiO_2$  are examined in the papers of V.V. Cergeyev

[81], Scharma [79], and other investigators [82].

At the Illinois Institute of Technology (USA), Mondolfo and Roy investigated the reduction of finely ground  $TiO_2$  that had been briquetted with aluminum powder when the briquettes were immersed in molten aluminum [72]. In this process, titanium dioxide containing 99.5%  $TiO_2$ , 0.5%  $SiO_2$ , 0.1%  $P_2O_5$ , 0.1%  $SO_3$  and 0.004-0.005%  $P_2O_3$  was ground to -0.5-1.5 mm and briquetted with 99.5% pure aluminum powder under a pressure of about 30 kgf/mm<sup>2</sup>. The briquettes, which contained no less than 50% Al, were submerged with agitation in aluminum that had been superheated to 1300-1400°C. This reduced the titanium to form a Ti-Al alloy in which aluminum oxide was dispersed. The charge composition was calculated to obtain more than 30% Ti in the alloy, since the melting point of the alloy rose sharply at higher contents and this made it difficult to separate the  $Al_2O_3$  from it. During reduction, the molten bath was flushed with argon or helium to facilitate floating and removal of the slag. Addition of about 1% (on the mass of the alloy) of cryolite to the charge slags out an additional amount of aluminum oxide. The best results were obtained in an induction furnace in a magnesium oxide crucible. The charge consisted of 1 kg of  $TiO_2$  and 4 kg of aluminum. Temperature 1400°C, smelting time 2 hours. This produced 3 kg of an alloy containing 27-30% Ti. The inventors of the method report that the oxide film formed on the surface of the fused aluminum protects the Ti-Al alloy from oxidation, so that the reaction can be conducted in open apparatus without an inert atmosphere. Analysis of the alloy produced in one of the experiments indicates that the alloy contained 8.5% titanium and 0.049% oxygen after slagging of the  $Al_2O_3$  and argon flushing of the bath; after remelting of the alloy under cryolite, its oxygen content was down to 0.007% (as we know, cryolite  $Na_2AlF_6$  is a good solvent for  $Al_2O_3$ ). The alloy can also be treated with a mixture of Ca +  $CaCl_2$  or remelted with a small amount of  $TiB_2$  to eliminate the oxygen.

Most of the experiments resulted in Ti-Al alloys containing 12 to 29% Ti. Such alloys cannot be used as structural materials and require further refinement to lower the aluminum content to

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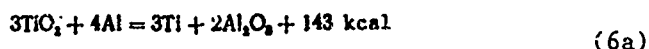
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6-8%. The ability of magnesium to dissolve up to 30% Al at 600-1000°C and the practically total insolubility of metallic titanium in liquid magnesium at these temperatures were utilized to separate the aluminum from the Ti-Al alloy [78]. The Ti-Al alloy was concentrated by cofusing it with magnesium in a magnesium oxide crucible at 550-1100°C. Solid Ti-Al particles settled in the resulting alloy, which has a lower melting point and density than the Ti-Al alloy. To prevent oxidation of the magnesium and contamination of the Ti-Al alloy with oxygen, the cofusion was carried out under a cover flux or in an argon atmosphere. However, the process became difficult to manage when the oxide-saturated flux became heavier than the Mg-Al alloy and lost its covering properties. Zinc was added to increase the weight of the Mg-Al alloy formed on cofusion of the Ti-Al alloy with the magnesium; this prevented the cover flux from sinking. On completion of cofusion, the melt was allowed to settle for a few minutes to separate it into layers and permit pouring off the Mg-Al-Zn alloy. To enrich the Ti-Al alloy from 12-29 to 92% Ti and up, it was treated with an Mg-Zn alloy no fewer than 7 times in succession. The final product was found to contain less than 0.001% Zn on leaching with Mg-Zn alloy. After cofusing with Mg-Zn alloy and removal of the resulting new Mg-Al-Zn alloy and the flux, the Ti-Al alloy residue was treated with 10-20% hydrochloric acid or vacuum-distilled at 850°C and a residual pressure of 0.001 mm Hg to remove residues of magnesium and zinc from the Ti-Al alloy. In either case, the Ti-Al alloy contained less than 0.05% Mg after treatment. The best experiments produced a coarse Ti-Al alloy powder containing from 6.58 to 7.14% Al, 1.15-1.75% Fe, 0.42-0.72% Si, 0.047-0.052% O<sub>2</sub>, 0.002-0.003% N<sub>2</sub>, 0.001% Zn, 0.002-0.003% Mg, and 0.01% C.

Systematic studies of the aluminum reduction of TiO<sub>2</sub> were carried out in 1957 by N.N. Murach and V.G. Musiyenko [72]. The material reduced was technical titanium dioxide, and the reducing agents were types PA-1 and PA-3 aluminum powders [55]. The open metallothermic process was conducted in a graphite-fireclay crucible [76].

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The thermochemical equation of the aluminothermic reduction of  $TiO_2$



indicates that 597 kcal of heat are liberated on reduction of 1 kg of  $TiO_2$ . It has been established that the minimum theoretical amount of heat  $Q$  that must be liberated in the charge for Reaction (6a) to occur spontaneously is determined by the relation

$$\log Q = \frac{\Delta H_{298}^0}{257} + 1.92 \quad (7)$$

and amounts to 592 kcal/kg ( $\Delta H_{298}^0 = 219 \text{ kcal/mole}$ ).

Since an additional 9.5 kcal/g-atom of titanium is released on formation of the Ti-Al alloy [83], the heat effect of reaction (6a) is sufficient to support spontaneity.

However, according to the authors of [72], the charge must contain 1350 kcal per kg of reducible oxides to ensure that the reaction will go to completion, to melt the slag, and to produce a uniform regulus. Bertholet's salt was introduced into the charge as a warming additive to raise its heat content to this figure, and  $CaF_2$  and  $CaCl_2$  to lower the viscosity of the slag.

A charge of the indicated composition was placed in a graphite-fireclay crucible, compacted, and fired with an igniting mixture consisting of fine aluminum and ferric-oxide powders or Bertholet's salt mixed with aluminum. The reaction propagated rapidly throughout the entire volume of the crucible after ignition, and the process was completed after 1-2 minutes for a charge of about 10 kg. This gives the regulus time to form an ingot on the bottom of the crucible, suppressing the interaction of the alloy with the acid slag and atmospheric oxygen. The slag is easily removed from the alloy after the crucible has cooled to room temperature.

In these experiments, the best results were obtained at the optimum 1250-1350-kcal-per-kg heat content of a charge containing a 10-25% reducer excess. The moisture content must not exceed

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TABLE 31  
Titanium Content in Alloy and Percentage Extraction of  
Titanium from Raw Material as Functions of  
Charge Composition

| Charge composition, parts (by mass) |          |                                |                  | Titanium<br>content<br>in alloy,<br>% | Extraction<br>of titanium<br>from raw<br>material, % |
|-------------------------------------|----------|--------------------------------|------------------|---------------------------------------|--|
| TiO <sub>2</sub>                    | Al       | K <sub>2</sub> CO <sub>3</sub> | CaF <sub>2</sub> |                                       |  |
| 1                                   | 0.75     | 0.65                           | 0.45             | 70                                    | 55-57  |
| 1                                   | 0.9      | 0.78                           | 0.53             | 65                                    | 60-62  |
| 1                                   | 0.95-1.0 | 0.73-0.75                      | 0.5-0.53         | 65                                    | 62-65  |
| 1                                   | 1.0-1.06 | 0.75-0.77                      | 0.5              | 55                                    | 60-61  |
| 1                                   | 1.3-1.35 | 0.85-0.87                      | 0.53             | 40                                    | 57-60  |
| 1                                   | 1.5      | 0.9-1.0                        | 0.57             | 35                                    | 51-55  |

1.0% in the Bertholet's salt or 0.1% in the TiO<sub>2</sub>, CaO<sub>2</sub>, and CaF<sub>2</sub> in order to prevent the melt from erupting from the reaction crucible.

The toughest ingot, and the one most easily separated from the slag, is obtained by reducing a charge designed to produce an alloy with 60-65% Ti.

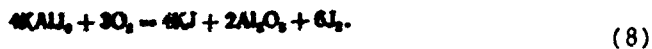
It was also established that large single melts are not advantageous, since the slag and alloy formed at large charge weights harden very slowly. This promotes the reaction between the slag and the alloy, which contaminates the alloy with oxygen. Thus, other conditions the same, the alloys contained 2-5% oxides when a mass smaller than 10 kg was melted, and 12-25% for a 30-kg mass. This is the essential drawback of the aluminothermic process.

The results of experiments conducted under the conditions described and with charges of various compositions are assembled in Table 31.

The alloys obtained by the authors of [72] contained about 65% Ti, 30% Al, remainder insoluble residue consisting chiefly of the oxides of aluminum, calcium, silicon, etc.

Alloys of the compositions listed in Table 31 can be used as masters for introduction of nonferrous and rare metals into alloys and (after special purification) as raw materials for the manufacture of structural Ti-Al alloys.

One example of such purification is found in Blumenthal's proposal [71] for iodination of the alloy by iodine dissolved in carbon disulfide. This forms  $TiI_4$  and  $AlI_3$ , which dissolve completely in carbon disulfide on boiling. After the carbon disulfide has been distilled off, the  $TiI_4$  and  $AlI_3$  crystals are mixed with KI and heated to form nonvolatile  $KAlI_4$ , and the titanium tetraiodide, which does not form binary salts with alkali metals, is distilled out of the reaction mass in a special vacuum apparatus. The  $TiI_4$  obtained in this way is dissociated thermally in a vacuum on a titanium filament that has been heated to 1300-1500°C. The iodine that is released is returned for use in iodination of Ti-Al alloy. Moreover, the iodine and KI can be regenerated from the  $KAlI_4$  by passing dry hot air through it. The reaction is



About 98% of the iodine is regenerated in this way.

The titanium and aluminum iodides can also be separated by vacuum rectification or distillation. The large difference between the melting points of  $TiI_4$  (150°C) and  $AlI_3$  (191°C) aids in distilling the  $TiI_4$  out of the solid  $AlI_3$  in a vacuum at 160-180°C.

In another proposed method, the Ti-Al alloy is processed by leaching out with aqueous alkali solution.<sup>5</sup> According to the reported results, it was possible to obtain a powder with 97% Ti, 2% Al, and 1.2%  $O_2$ , and, after treatment of this alloy with sulfuric acid and water washing, even with oxygen contents as low as 0.3%. However, N.N. Murach and V.G. Musiyenko established that aluminum cannot be removed by this method from the resulting Ti-Al alloy, which contains 40-65% Ti [73].

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Nowotny and Baldwin<sup>6</sup> proposed a method for separation of Ti-Al alloy in which the Ti-Al alloy is ground to 1 mm and a mixture of  $\text{AlCl}_3$  vapor with a carrier gas (for example, hydrogen) is passed through the Ti-Al alloy at a mixture pressure of about 160 mm Hg and a temperature of about 1300°C. It is recommended that the process be conducted in a column, with the gas fed in at the bottom through a layer of the crushed alloy. On cooling in a condenser, the aluminum subchloride ( $\text{AlCl}$ ) vapor, which is formed in a mixture with  $\text{H}_2$ , decomposes with formation of Al and  $\text{AlCl}_3$ , which are recycled after separation [74]. The method is said to eliminate all of the aluminum from the alloy.

The potentially most attractive method of separating the Ti-Al alloy and purifying the titanium of oxygen and other harmful impurities is electrolytic refining, in which the crude Ti-Al alloy is subjected to anodic solution in a fused electrolyte consisting basically of alkali- and alkaline-earth chlorides and titanium, and whose development is now being pushed vigorously in a number of countries. During electrolysis, a Ti-Al alloy that contains practically no oxygen is deposited at the cathode. After separation of the cathodic deposit from the electrolyte and remelting in vacuum-arc furnaces, this alloy can be used as a high-grade structural material.

A method in which aluminothermic reduction of  $\text{TiO}_2$  is combined with subsequent electrolytic refining of the crude alloy may, assuming that a high-output, operationally efficient electrolyzer is developed, become one of the basic industrial processes of titanium production and one that might compete with the methods in extensive use at the present time — the magnesiothermic and sodiothermic processes.

Footnotes

- | Manu-<br>script<br>Page<br>No. |   |
|--------------------------------|---|
| 238                            | <sup>1</sup> Patent (USA), No. 2,850,379, 1958.   |
| 241                            | <sup>2</sup> See also Patent (Brit.) No. 675,933, 1952; Patents (USA) Nos. 2,904,428, 1959; 2,830,893, 1958; 2,834,667, 1958. |
| 242                            | <sup>3</sup> Patents (West German), Nos. 1,067,699, 1960; 961,761, 1958.  |
| 244                            | <sup>4</sup> Patent (Brit.), No. 761,750, 1956.   |
| 248                            | <sup>5</sup> Patent (Brit.), No. 733,712, 1955.   |
| 249                            | <sup>6</sup> Patent (Australian), No. 194,615, 1958.  |

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## Chapter 13

### REDUCTION OF TITANIUM TETRACHLORIDE BY MAGNESIUM

#### Developmental History of the Magnesiothermic Method

Magnesium is one of the most widely distributed elements in nature. Its content in the earth's crust is 2.35%. In the table of abundances of the elements in the earth's crust, magnesium comes after oxygen, silicon, aluminum, iron, calcium, sodium, and potassium.

The factors behind the production of magnesium on a large industrial scale are the large deposits of magnesium raw materials, a highly productive technology for producing the metal by electrolysis, and its comparatively low cost.

In 1966, world magnesium production (outside of the USSR) came to something more than 100 thousand tons per year. The purity of magnesium produced by the electrolytic process is quite high (~99.9%).

Magnesium is distinguished by a strong affinity for chlorine ( $-\Delta Z_{1073}^0 \text{MgCl}_4 = 55 \text{ kcal/g-atom of chlorine}$ ), which is 12.0 kcal/kcal/g-atom of chlorine higher at 800°C than the affinity of titanium for chlorine ( $-\Delta Z_{1073}^0 \text{TiCl}_4 = 43 \text{ kcal/g-atom of chlorine}$ ); this is quite enough for complete reduction of  $\text{TiCl}_4$  by magnesium. The relation of the melting and boiling points of magnesium and the  $\text{MgCl}_2$  formed as a result of the reduction favor conduct of the

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process in the 720-900°C temperature range. Magnesium and titanium are practically insoluble in one another.

All of this, together with the technological features of the titanium-reducing process, make magnesium one of the most advanced reducing agents for large-scale production of titanium sponge by the magnesiothermic method.

The first experiments in the reduction of titanium tetrachloride by magnesium filings in carbon dioxide were made as early as 1892 [89]. However, carburization of the metal made it impossible to obtain titanium of satisfactory purity.

The next attempt to reduce titanium tetrachloride with magnesium was made by the American investigator Kroll, who took out a US Patent in 1940 for a magnesiothermic method of titanium production [90, 111].<sup>(1)</sup>

Kroll conducted scaled-up laboratory experiments. The internal surface of the reactor was faced with molybdenum to prevent the  $TiCl_4$  and titanium from reacting with the reactor material. The process was conducted in an atmosphere of purified argon in the temperature range from 850 to 950°C with holding at 1060°C at the end of the process. The reaction mass obtained was leached with dilute hydrochloric acid solution and water. These experiments represented the first use of the magnesiothermic method to produce titanium with room-temperature plasticity.

Kroll's researches formed a basis for expanded experimentation and improvement of the process. Beginning in 1942, the US Bureau of Mines sponsored extensive semiindustrial experiments at an installation at Boulder City (Nevada). They established the possibility of conducting the process at 750-900°C in a low-carbon-steel reactor with subsequent purification of the reaction mass by vacuum separation. Research on the magnesiothermic method became a matter of particular urgency beginning in 1946 with the rapid development of jet aviation, which required substantial quantities of light heat-resistant alloys based on titanium. In 1946-1949, the production of titanium sponge at the Boulder City installation was brought up to 100 kg per day, and a pilot plant

Footnote (1) is on page 305.

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with a daily sponge output of 750 kg was built around this installation in 1952 [91, 92].

Successful mastery of the magnesiothermic method enabled the USA to begin a broad program aimed at developing a titanium industry.

The reasons why this program was not implemented were cited in Part I.

Production of sponge titanium was organized in the early '50's in the Soviet Union. The USSR's titanium industry is a major contemporary division of the socialist economy. The production of titanium sponge in the USSR is rising steadily and rapidly with the planned socialist economy as a base.

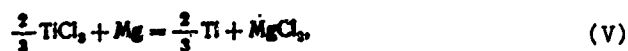
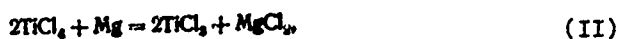
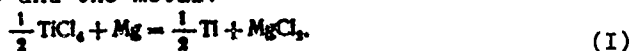
#### Physicochemical Fundamentals of the Reduction

By analogy with complex reactions that proceed via intermediate compounds, the reduction of titanium can be represented as stepwise reduction of titanium tetrachloride and the lower chlorides:



As a convention, the reactions that take place here can be broken down into two groups:

A. The reactions in which titanium tetrachloride is reduced to the lower chlorides and the metal:



B. Secondary reactions involving titanium tetrachloride and

products of the group A reactions, and the disproportionation reactions of the lower titanium chlorides:



etc.

The thermodynamic probabilities of the reaction in which  $\text{TiCl}_4$  is reduced by magnesium and those of the secondary reactions of  $\text{TiCl}_4$  with the reduced titanium have been the subject of many studies [1, 128, 136, 138-140].

However, only particular cases of the interaction were examined in the work of S.F. Belov and S.I. Sklyarenko [136, page 72], Kubaschewski [137], V.A. Ryabov, G.N. Zviadadze, and others [87, 138-140].

R.A. Sandler made a systematic study of the chemical mechanism of the reduction reaction, computing the isobaric-isothermal potential changes for all reactions possible in reduction [128]. The calculations were made in the 650-1050°C temperature range for the reactions that take place in the condensed and gaseous phases, and for the first time in the case of the latter. Analysis of the results and determination of reaction-mass chemical compositions led R.N. Sandler to the following conclusions:

1. When gaseous  $\text{TiCl}_4$  reacts with liquid magnesium, reactions (I-VI) are thermodynamically possible. Reaction (IV), which proceeds with formation of  $\text{TiCl}_2$ , involves the largest loss of free energy; it is followed in order of free-energy loss by reactions (III), (I), (II), and (V). Among the secondary reactions, that of  $\text{TiCl}_4$  with titanium (VIII), which also forms  $\text{TiCl}_2$ , is the most probable in this case.  $\text{TiCl}_2$  can be identified in samples of magnesium chloride taken during the reduction process;  $\text{TiCl}_3$  is not detected in such samples.

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2. For the gaseous-phase reactions, (III) and (II), which form  $TiCl_2$  and  $TiCl_3$ , are most probable. Reaction (II) is improbable from the kinetic standpoint.

3. Formation of magnesium subchloride  $MgCl$  simultaneously with that of  $MgCl_2$  is a possibility during the reduction process. The standard enthalpy and entropy of the subchloride, calculated by the thermochemical rule of logarithms, are minus 66.8 kcal/mole and 1.90 cal/(deg·mole), respectively. Magnesium subchloride is unstable under standard conditions, but it is identified in the gaseous phase at high temperatures [128, 129]. It has been established that the thermodynamic probability of reactions leading to formation of magnesium subchlorides is quite high in the temperature range from 650 to 1050°C.

Figure 37 shows our calculated temperature curves for the isobaric-isothermal potentials of the reactions examined above. The starting data were those of Table 29. The temperature curves of reaction free energy were calculated by the method described in Chapter 11.

As we see from Fig. 37, all of the reactions considered, except for (IV), (VIII), and (IX) are possible from the thermodynamic standpoint at temperatures above 1100-1300°C in the reduction of titanium tetrachloride by magnesium.

To arrive at a more correct judgment as to the chemical mechanism of the reduction process, it is necessary to consider the physicochemical effects that accompany it; foremost among these are chemical equilibria, the physical states of the substances

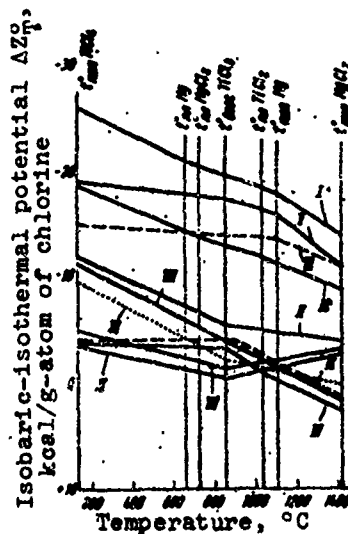


Figure 37. Temperature curves of isobaric-isothermal potentials for the reactions of magnesiothermic reduction of titanium chlorides.

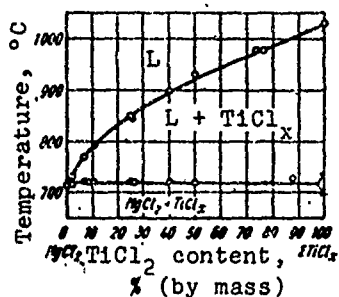


Figure 38. Phase diagram of MgCl<sub>2</sub>-TiCl<sub>2</sub> system.

(by mass) (Fig. 38). It was also found that salt mixtures containing lower chlorides of titanium and at equilibrium with metallic titanium contain only TiCl<sub>2</sub> and no TiCl<sub>3</sub>. Titanium trichloride does not dissolve in appreciable quantities in magnesium chloride. On the basis of these experiments, the authors are inclined to the view that the reduction process takes place in stages with the formation of titanium dichloride as the result of the primary reaction.

According to A.I. Zhurin [143] and I.G. Bukun and Ye.A. Ukshe [144], the solubility of magnesium in MgCl<sub>2</sub> is 0.25-0.40% in the 800-1200°C temperature range. This fact may influence the course of the reactions that take place in the fused magnesium chloride and at its interface with the gaseous phase, which contains TiCl<sub>4</sub> vapor.

According to K.T. Aust and I.M. Pidznen [145], the solubility of titanium in magnesium is only 0.006% at 700°C and 0.015% at 850°C. Magnesium is practically insoluble in titanium. Thus, these factors cannot significantly influence the course of the reduction process.

The surface phenomena that accompany the reduction of TiCl<sub>4</sub> by magnesium were studied by G.V. Forsblom and Ye.G. Goldelenok [146]. It was established that magnesium does not wet a clean steel reactor surface or titanium at 650-900°C.

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participating in the reactions, the mutual solubilities of these substances, surface phenomena, the rates of the various processes, etc.

K.I. Komarek and R. Gerasimenko [142] studied the equilibrium between metallic titanium and the solution of TiCl<sub>2</sub> in magnesium chloride. It was established that the MgCl<sub>2</sub>-TiCl<sub>2</sub> system has a peritectic with a melting point of 716°C at a TiCl<sub>2</sub> content of 0.35%

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Under conditions approaching those obtaining in an industrial reactor after the first batches of  $TiCl_4$  have been loaded into it, molten magnesium wets the surfaces of a steel reactor and titanium sponge quite well and may, under the influence of surface forces, climb the vertical steel or titanium-sponge-coated walls of the reactor. Fused magnesium chloride thoroughly wets the surface of molten magnesium and coats it with a continuous film. In the opinion of G.V. Forsblom and Ye.G. Gopiyenko, this may break contact between the magnesium and the  $TiCl_4$  in the reduction process and lower the reaction rate. They also established that in the presence of magnesium chloride, metallic magnesium wets titanium sponge better than does magnesium chloride. This indicates that the presence of  $MgCl_2$  does not block penetration of the metallic magnesium into the pores of the sponge or interfere with its ascent through capillaries in the zones of the reactor above melt level. According to V.A. Zhivov, magnesium rises to a maximum height of 13 cm above melt level when the sponge-capillary diameter is 0.5 mm [147]. With rising temperature, the wetting of titanium and steel by metallic magnesium and its chloride is improved.

The temperatures of physical-state changes of the substances that participate in the reduction process and their vapor pressures at various temperatures are given in Tables 29 and 30. It has been established by experiment and calculation that the rate of evaporation of magnesium substantially exceeds that of  $TiCl_4$  [130]. Thus, the rate of evaporation of magnesium from an exposed surface cannot inhibit the reduction reaction, but during the process, especially if the reactor contains a large amount of sponge and magnesium chloride, the conditions for vaporization of the metal may deteriorate sharply, and the limiting factor may be the rate of transport of magnesium to the evaporation surface or into the zone of the reaction with the titanium chlorides, rather than its evaporation rate.

Although the mechanism of titanium tetrachloride reduction and formation of titanium sponge has been studied by many investigators, there is as yet no clear consensus regarding this

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process with adequate theoretical and practical confirmation, owing to its complex nature.

One of the first studies of the mechanism of the magnesio-thermic titanium reduction is due to Wartman et al. [133]. The experiments were run in a reactor 254 mm in diameter at 800°C. The variable factor was the total amount of  $TiCl_4$ , which ranged from 5 to 60% of that theoretically needed to utilize all of the magnesium loaded into the reactor. When the specified amount of titanium tetrachloride had been fed in, the reactor was cooled and open for study of the composition of the reaction mass and its distribution through the volume of the reactor.

It was established that at the start of the process, the reduction reaction takes place on the surface of the molten magnesium, which gradually becomes covered by a film of the magnesium chloride that is formed, which wets the magnesium well. The film makes it difficult for the magnesium to contact the  $TiCl_4$  and prevents further reaction on the magnesium surface. At this time, the reaction front shifts toward the reactor walls, where the conditions for the reaction of  $TiCl_4$  with magnesium are more favorable owing to drainage of the salt from the surface of the magnesium, which is raised up the walls of the reactor or capillaries in the sponge formed on the walls as a result of surface tension or capillary forces. Subsequently, in Wartman's opinion, the reactions take place for the most part on the reactor walls or on the sides of the sponge as it grows from the sides toward the center of the reactor.

At low temperatures and  $TiCl_4$  infeed rates, a so-called "bridge" of titanium sponge may form above the liquid-phase level, filling the entire cross section of the reactor and interfering with transport of magnesium into the reaction zone. Actually, in none of Wartman's experiments was a layer of titanium sponge unconnected to the walls found on the bottom of the reactor.

To determine the possibility of running the reaction in the gaseous phase, the reactor was fitted with special rods, some of which were welded to its bottom with their ends projecting out of

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the fused bath into the reactor's gas space, while others were welded vertically to the reactor cover and accommodated entirely in the gas space, without coming into contact with the fused magnesium. It was found that titanium sponge formed on the rods projecting out of the melt after TiCl<sub>4</sub> was supplied, while the rods that were entirely in the gaseous phase grew no sponge. On this basis, Wartman concluded that the reaction does not take place in the gaseous phase.

Kroll, the originator of the magnesiothermic method, concurs with Wartman's conclusions as to the mechanism of the reduction process [131]; Gillemot, while supporting Wartman's position in its essentials, takes the view that the reaction occurs between molten magnesium and TiCl<sub>4</sub> vapor at the beginning of the process, but that when most of the reducer has been utilized and all of it is in the pores of the sponge that has formed, the reaction between TiCl<sub>4</sub> and magnesium proceeds in the gaseous phase [122].

V.A. Reznichenko and S.V. Ogurtsov [134; 65, page 82], working independently of Wartman, arrived at similar conclusions as to the mechanism of the reduction reaction. According to their studies, the molten magnesium does not wet the steel walls of the shell before TiCl<sub>4</sub> is admitted into the reactor. Immediately after a feed of TiCl<sub>4</sub>, the reaction occurs both in the gaseous phase and on the magnesium surface. Thereafter, the reaction between the titanium tetrachloride and magnesium vapor develops preferentially on the walls of the shell, where the available surface facilitates germination of the new phase, metallic titanium.

The walls of the shell then become coated with a thin layer of titanium, and a film of magnesium chloride forms on the magnesium surface, isolating the magnesium from reaction with TiCl<sub>4</sub>. The layer of titanium that has settled on the reactor walls and the film of magnesium chloride on the surface of the metal change the surface-force relationships: in this case, the magnesium now wets the titanium-coated walls of the shell quite well and rises on these walls above the melt level. Since the magnesium surface is coated with the magnesium chloride film, the reaction develops only where the magnesium surface is free of this film, i.e., on

the sponge-coated walls of the reactor. The lateral surface area of the sponge growing on the shell walls is small and coated entirely by the  $MgCl_2$  draining down it; the focus of the reaction persists only on the "crest" of the upward-growing sponge, from which the magnesium chloride drains. The higher the rate of  $TiCl_4$  supply, the larger will be the  $MgCl_2$ -coated lateral area of the sponge lining, and the more rapidly will the lining grow upward. But at a certain  $TiCl_4$  feed rate, the reduction may also take place on the lateral surface of the sponge lining. Thus, in the opinion of V.A. Reznichenko and S.V. Ogurtsov, the growth front of the titanium sponge is determined by the rate of  $TiCl_4$  supply. The distribution of the sponge over the various zones of the reactor can be controlled by varying the titanium tetrachloride flowrate.

In a study of the kinetics of the reduction process, V.A. Reznichenko and S.V. Ogurtsov established that as the  $TiCl_4$  flowrate is increased, the rate of the reduction reaction increases up to a certain value and then remains practically constant as the  $TiCl_4$  supply rate is increased further. At low  $TiCl_4$  supply rates into the reactor, the apparent activation energy is 25,700 kcal/mole, indicating that the reaction takes place in the kinetic region. Increasing the  $TiCl_4$  supply rate lowers the apparent activation energy to 10,750 kcal/mole with a simultaneous increase in the reduction rate. It was also found that the specific pressure  $p$  of the titanium tetrachloride is related to the  $TiCl_4$  supply rate  $v$  by the equation

$$p = av^n,$$

where  $a$  is the slope and  $n$  is an exponent, from which it becomes evident that the specific pressure in the system drops with increasing  $TiCl_4$  supply rate.

This indicates that processes that activate the reduction reaction take place in the system. In the opinion of the authors of [65] and [134], the activation is caused by heterogeneous catalysis. The catalyst is the surface of the titanium sponge, on whose active centers the titanium tetrachloride is adsorbed. The

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adsorbed  $TiCl_4$  molecules are more reactive than the  $TiCl_4$  molecules in the vapor or liquid state, because of stretching and weakening of the intramolecular bonds of the adsorbed  $TiCl_4$  molecules by adsorption forces. The weakening of the intramolecular bonds may be so substantial that the  $TiCl_4$  molecule dissociates to form lower titanium chlorides.

The presence of adsorbed  $TiCl_4$  molecules with enhanced reactivity on the active centers of the sponge causes the reduction reaction to take place preferentially on these centers, which are also crystallization centers for the reduced titanium particles.

In the opinion of V.A. Reznichenko and S.V. Ogurtsov, the increase in the reduction-reaction rate with increasing  $TiCl_4$  supply rate into the reactor results from greater volume and surface development of the sponge with increasing  $TiCl_4$  supply rate, so that the number of active adsorption and crystallization centers increases and, in turn, the reduction reaction is activated and accelerated. However, the same authors established that the reaction rate rises to a certain limit. This is explained by the fact that at a certain  $TiCl_4$  supply rate, the sponge reaches its maximum volumetric development and, consequently, the maximum possible number of active centers: as the  $TiCl_4$  supply rate increases further, therefore, the rate of the reaction itself remains constant.

The autocatalytic nature of the reduction reaction, activated absorption of  $TiCl_4$ , and crystallization of the reduced titanium particles on the active centers of the sponge are, in the opinion of these authors, the causes of the spongy structure of the resulting titanium.

This autocatalytic theory of the reduction mechanism cannot, however, adequately explain the multitude of processes that take place in the industrial reactor. Further, the authors of [65, page 82] leave out of consideration such important factors as the course of the reactions in the gaseous phase, the formation of lower titanium chlorides, the solubility of magnesium and the titanium chlorides in magnesium chloride, the role of surface

phenoema, their influence on adsorption, etc.

According to R.A. Sandler,<sup>(2)</sup> the mechanism of the reduction reaction cannot be autocatalytic because of the inhibition of the reactions at a certain  $TiCl_4$  supply rate; in autocatalysis, the reaction rates should rise without limit. R.A. Sandler explains the decrease in activation energy with increasing  $TiCl_4$  supply rate in terms of passage of the reaction from the kinetic to the diffusion region rather than by autocatalysis [308].

Another treatment has been advanced for the mechanism of the  $TiCl_4$  reduction process and sponge formation [130]. Studying the role of the reactions in the gaseous phase, R.A. Sandler established that the preferential development of the reactions in the gaseous or condensed phases is determined basically by the  $TiCl_4$  supply rate into the reactor, the partial pressure of the inert gas, and formation of intermediate titanium compounds. At low  $TiCl_4$  delivery rates (of the order of 5-10 g per  $cm^2$  of reactor cross section per hour) and a low inert-gas partial pressure (0.2-1.0 atm), the reactions take place substantially in the gaseous phase. Increasing the  $TiCl_4$  supply rate and inert-gas partial pressure inhibits the gas-phase reactions and promotes those that occur in the condensed phases. It has been established that the gaseous-phase reactions take place stepwise with formation of the intermediate lower chlorides  $TiCl_2$  and  $TiCl_3$ .

The hypothesis of stepwise advance of the reactions was advanced by V.Yu. Kramnik [106, page 14]. It was also found that when the reactions take place in the gaseous phase, the reduced titanium forms a fine powder that cannot be shaped into a massive block of titanium sponge such as usually forms in the reactor.

A block of sponge may be formed when the reduction reactions take place for the most part in the condensed phases.

A study of the reactions proceeding in the condensed phases that was undertaken by R.A. Sandler led him to the conclusion that the reactions in which  $TiCl_4$  is reduced to  $TiCl_2$  and to metallic titanium, i.e., Reactions (III) and (VI), take place preferentially in these phases. The  $TiCl_2$  formed in the first stage of

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the reduction dissolves in the  $MgCl_2$  and is further reduced there by the magnesium. Further reduction takes place basically on the surfaces of previously reduced titanium particles, so that these particles grow. Settling to the bottom of the reactor, the aggregated titanium particles form the sponge block.

For Reaction (III), the resulting stoichiometric melt contains about 55%  $TiCl_2$  and crystallizes at  $920^\circ C$ . If the temperature is lowered below  $920^\circ C$  in one of the reactor's zones, the  $TiCl_2$  precipitates from solution, and since the reactor walls are most often supercooled, it is here that most of the  $TiCl_2$  crystallizes. Rising along the reactor walls or capillaries in the sponge lining, the magnesium reduces the  $TiCl_2$  further to the metal, so that the sponge on the reactor walls grows. This is confirmed in industrial practice: when the wall temperature is lowered, the sponge lining grows more rapidly, while at temperatures above  $930-940^\circ C$ , little sponge growth occurs on these walls.

Increasing temperature and precipitation of  $TiCl_2$  into the solid phase increase the probability of the secondary reaction of  $TiCl_4$  and  $TiCl_2$  (X), which forms volatile  $TiCl_3$ ; the latter condenses in the cold zones of the reactor, where it can be further reduced by magnesium vapor.

Although R.A. Sandler's conclusions as to the reaction mechanism do not take account of all processes taking place in the reactor, they are consistent with certain facts observed under industrial conditions. For example, certain of these inferences are in good agreement with the results of experiments made on industrial reactors by E.Ye. Lukashenko et al. [106, page 14].

E.Ya. Lukashenko et al. studies the influence of the degree of  $TiCl_4$  and magnesium utilization on the reduction process, sponge formation, and reaction-mass composition. The experiments were run at temperatures of  $920-960^\circ C$ , an argon pressure of 0.2 atm, and a rate of  $TiCl_4$  supply into the reactor of  $8-12 \text{ g}/(\text{cm}^2 \cdot \text{h})$ . The titanium tetrachloride was fed into a reactor with a shell insert until 10, 20, 40, 50 and 60% of the theoretically possible amount of magnesium had been utilized. After the specified amount

of  $TiCl_4$  had been supplied to the reactor, the magnesium chloride and magnesium were decanted, the reactor was cooled, and the distribution of the reaction products in the volume of the reaction shell was investigated.

E.Ye. Lukashenko's experiments indicated that the first stage of the reduction process (utilization of the magnesium to 20-40%) is characterized by formation of a central sponge block. The lining on the reactor walls grows only insignificantly; its position is higher than the original level of the fused magnesium in the reactor. During the first phase, the reaction takes place on the horizontal melt surface. In the opinion of the authors, wetting of the reactor walls by the magnesium and capillary effects in the sponge liner are not significant for the process in the initial phase. The magnesium chloride film on the magnesium surface does not inhibit the reaction with the reducing agent and is not an obstacle to transport of magnesium into the reaction zone, since the metal is transported through capillaries in the minute titanium particles that float on the melt surface. In the course of the reduction, these particles become larger and drop to the bottom of the reactor, forming a porous central sponge block.

During the second phase (40 to 50% utilization of the magnesium), there is no substantial change in the nature of the reduction and sponging processes, the process rate remains high, and the sponge forms for the most part as a central block under a layer of melt.

During the third phase (more than 50% magnesium utilization), the sponge liner begins to grow rapidly and the rate of the process falls off.

The explanation offered for this by the authors of the study is that in the last phase, practically all of the magnesium is in the pores of the sponge and the rate of its transport into the reaction zone is determined to a substantial degree by surface phenomena and capillary and diffusion processes. Since the most favorable conditions for transport of magnesium are created at the reactor walls and on the surface of the sponge liner during

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this period, the reaction is displaced into these zones and the liner begins to grow rapidly. It was established that the reaction occurs not only on the surface of the sponge and the sponge liner, but also in the layer of fused magnesium chloride. This is explained by further reduction of lower titanium chlorides dissolved in the  $MgCl_2$ . The compacting of the central sponge block that is observed in practice during the last stage of the reduction process and the periodic temperature rises in various zones of the reactor, including the interior of the melt, are also explained by further reduction of lower titanium chlorides in the fused magnesium chloride.

Analysis of the experimental data discussed above, the physicochemical peculiarities of the heterogeneous system, the temperature curves of the reduction-reaction isobaric-isothermal potentials, and observations of the processes under industrial conditions permit the following inferences as to the mechanism of magnesiothermic reduction of titanium tetrachloride and titanium-sponge formation.

Immediately after  $TiCl_4$  is fed into a reactor containing molten magnesium at 650-900°C, the process takes place for the most part in the gaseous phase between titanium tetrachloride and magnesium vapors. The reaction between liquid magnesium and  $TiCl_4$  vapor is generally difficult during this phase owing to the extremely thin film of magnesium oxide on the surface of the reducer, which makes contact between the reagents difficult.

From the thermodynamic standpoint, the most probable reactions in the gaseous phase during the initial period are that of direct reduction of  $TiCl_4$  to the metal (I) and that of stepwise reduction of  $TiCl_4$  to the metal by way of the intermediate compound  $TiCl_2$  (III), (VI); reduction of  $TiCl_4$  to the metal via  $TiCl_3$  (II), (V) is less probable.

From the kinetic standpoint, on the other hand, the reaction in which  $TiCl_4$  is reduced to the metal via  $TiCl_2$  (III, VI) is most probable. The simultaneous triple collision of reagent molecules necessary for reactions (I) and (II) to take place in

the gaseous phase is improbable. Thus, the reactions in which  $TiCl_4$  is reduced stepwise via  $TiCl_2$ , (III) and (VI), are obviously preferred in the gaseous phase during the initial period of the reduction.

The initial period is characterized by a low  $TiCl_4$  flowrate (6-8 g per square centimeter of reactor cross section per hour) and a periodic pressure rise in the reactor, which must be controlled by bleeding vapor-gas mixtures; the temperature in the reactor is unstable and often rises abruptly in the upper zones and at the cover of the reactor.

The appearance of metallic titanium and magnesium chloride in the reactor changes the mechanism of the reduction process abruptly and determines the inception of the second, principal period of this process. The minute particles of reduced titanium formed during the initial phase (sizes about 500 Å) and the magnesium chloride settle onto the melt surface and the walls of the reactor. The titanium particles are held on the melt surface by surface-tension forces. The films of magnesium chloride and oxide that coat the magnesium surface break up, and the magnesium, wetting the titanium particles, rises and comes into contact with the titanium tetrachloride vapor.

Since the titanium particles originally formed have high surface activity and promote contact between the magnesium and  $TiCl_4$ , the reactions take place for the most part on the active centers of these particles, so that they grow rapidly. When the weights of the growing titanium aggregates come to exceed the surface tension forces, they settle onto the floor of the reactor and form a central spongy-structured block together with the metal previously deposited. At a certain temperature gradient at the reactor wall/fused bath interface, the titanium can crystallize on the reactor walls, with the result that they become lined with the metal. The appearance of this lining facilitates transport of magnesium into the reaction zone by capillary and surface forces, so that growth of the lining continues.

The presence of the minute titanium particles on the melt surface and reactor walls may result in adsorption of titanium

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chlorides on their active zones and a resulting increase in the reactivity of the chlorides. Thus, the appearance of titanium particles increases the reaction surface and the reactivities of the reagents; this accelerates reduction. Increasing the  $TiCl_4$  flowrate increases the number of active reaction and crystallization centers, and reaction rate rises accordingly. At a certain  $TiCl_4$  flowrate, there comes a point at which the rate of formation of titanium particles comes to equal the rate at which they settle to the reactor floor, and this would obviously cause stabilization of the reaction rate as the flowrate of  $TiCl_4$  into the reactor is increased still further.

From the thermodynamic standpoint, the most probable reactions, given adequate contact between the molten magnesium and the  $TiCl_4$  vapor, are those of direct reduction of  $TiCl_4$  to the metal (I) and stepwise reduction of  $TiCl_4$  to  $TiCl_2$  and to the metal (III) and (VI). Solution of  $TiCl_2$  in the magnesium chloride at the process temperature contributes to the progress of (III). The thermodynamic probability of the reduction of  $TiCl_4$  to titanium trichloride (II) is lower than that of reaction (III), but reaction (II) is promoted by the high volatility of  $TiCl_3$  at the process temperature. The  $TiCl_3$  that forms is removed from the reaction zone and condenses in the cold zones of the reactor.

Thus, given a sufficient amount of magnesium in the reactor, vitiation of the factors that impede its transport into the reaction zone, and the absence of contact between  $TiCl_4$  vapor and titanium-sponge surface that is uncoated by magnesium or magnesium chloride films, preference should be given to the direct reduction of  $TiCl_4$  vapor by molten magnesium to the metal (I) and stepwise reduction of  $TiCl_4$  by molten magnesium to  $TiCl_2$  (III), and then to titanium (VI). This period continues until about 40-50% of the magnesium loaded into the reactor has been utilized. It is characterized by a high  $TiCl_4$  consumption rate and relatively stable temperature and pressure of the vapor-gas mixture in the reactor.

If the reactor walls are not undercooled, the sponge forms for the most part as a central block and the liner is weakly

developed.

After magnesium utilization has reached 40-50%, the third period of the process begins. During this period, the proportions of magnesium and reduced sponge titanium in the reactor are such that practically all of the reducer is in the sponge pores. The rate of the process comes to be limited by the rate of magnesium transport to the reaction zone. During this time, the most favorable conditions for magnesium transport prevail at the reactor walls, which are coated with the titanium-sponge lining, through whose capillaries most of the reducing agent is transported into the reaction zone. The reaction proceeds chiefly on the surface of the sponge liner, and the liner therefore grows rapidly.

Apart from surface and capillary phenomena, the processes taking place in the fused magnesium chloride are also obviously of great importance during this period. As we noted earlier, the stepwise course of the reactions is associated with the preferential formation of  $TiCl_2$  in an intermediate stage. Moreover, when the titanium-sponge liner, which is in contact with the  $TiCl_4$  vapor, has developed, a secondary reaction between titanium and  $TiCl_4$  becomes possible, with the result that  $TiCl_4$  is reduced for the most part to  $TiCl_2$  (VIII). At the temperature of the process, titanium dichloride is highly soluble in  $MgCl_2$ , unlike  $TiCl_3$ , which is practically insoluble in  $MgCl_2$ . Titanium dichloride dissolved in magnesium chloride is reduced in the melt by the magnesium in the open pores of the sponge, which wets its surface, and by magnesium dissolved in  $MgCl_2$ .  $TiCl_2$  may be reduced at the surface of the sponge in the melt, and especially on the surface of the central block, with the result that the density of the block increases.

The vigorous progress of the reactions in the melt is confirmed by a fact of industrial practice: when the zone of maximum temperatures has shifted into the reactor zone below melt level, the rate of the process remains quite high. The abrupt temperature rise in various zones of the melt is obviously explained by crystallization of  $TiCl_2$  on the sponge surface at points at which it is locally undercooled and by vigorous further reduction of

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TiCl<sub>2</sub> to the metal in this zone when it contacts magnesium.

Toward the end of the process, the shortage of magnesium and the presence of a developed titanium surface in the reactor contribute to secondary reactions of TiCl<sub>4</sub> with titanium and with the lower chlorides. At 650-850°C, the secondary reactions (VIII), (VII), and (X) are thermodynamically most probable.

The culminating fourth period of the process intervenes when more than 50-60% of the Mg have been used. By this time, most of the unutilized magnesium is in pores in the titanium sponge and access of titanium chlorides to it is difficult. For this reason, the process slows down and is characterized by temperature instability, high pressure, and a low TiCl<sub>4</sub> consumption rate. When more than 60-70% of the Mg in the reactor has been used, the principal reactions are those of reduction of TiCl<sub>4</sub> to the lower chlorides and the secondary reactions, which also result in formation of lower titanium chlorides, with their inhibiting effect on further refinement of the reaction mass. This lowers the quality of the titanium and is detrimental to utilization of the titanium tetrachloride. Under industrial conditions, therefore, the utilization of the magnesium originally placed in the reactor does not usually exceed 60-70%.

The hypotheses that have been advanced regarding the mechanism of magnesiothermic TiCl<sub>4</sub> reduction cannot explain all of the varied physicochemical processes that occur in the real reactor, which constitutes a complex heterogeneous system that is not even at equilibrium. The preferential progress of specific reactions and the mechanism of sponge formation depend on temperature, the pressure of the vapor-gas mixture, TiCl<sub>4</sub> flowrate, magnesium utilization, heat-offtake conditions, the distribution of micro- and macrozones, interaction between the reagents and reaction products, and many other factors that are difficult to take into account. Reactions may take place simultaneously in all phases in the reactor, may be direct or secondary, etc. However, the processes take the general trends described above in the characteristic periods that we have discussed.

### Reactor and Reduction-Furnace Designs

The reduction of titanium tetrachloride by magnesium is accompanied by the liberation of a large amount of heat. The enthalpy of the over-all reaction [1] under standard conditions is 123.6 kcal/g-atom of titanium. In modern reactors for the  $TiCl_4$  reduction by magnesium, the heat-release rate is about 100-200 thousand kcal/h. Much of this heat must be withdrawn from the reactor.

The volumetric proportions of titanium, magnesium, and magnesium chloride in the reactor are such that there are 2.8 volume units of magnesium and 10.4 volume units of newly formed magnesium chloride to each unit volume occupied by titanium. For more complete utilization of the working reactor volume, therefore, the magnesium chloride must be drained periodically from the reactor during the reduction process.

At the present time, cylindrical reactors from 850-1000 to 1300-1500 mm in diameter and 1800-2000 to 3000 mm high are used as reducing reactors under industrial conditions. The diameter of a reducing reactor is basically limited by the demands of the next process -- vacuum separation of the block of reaction mass, where an increase in reactor diameter beyond a certain value is detrimental to heating of the reaction mass and sublimation of the magnesium and magnesium chloride residues out of the deep layers of the titanium sponge.

The first reduction of  $TiCl_4$  by magnesium was carried out at 850-1060°C in a reactor made from chrome-nickel steel and lined internally with sheet molybdenum [111]. The molybdenum sheet was intended to protect the chrome-nickel steel from reacting with the  $TiCl_4$  and magnesium. The second function of this lining was to provide conditions for running the reaction at the highest possible temperature in order to increase reactor productivity. However, reactors of this type did not come into industrial use because of the complexity of their manufacture and their high cost.

Later, as the magnesiothermic process was improved, reactors made from low-carbon, chrome-nickel, and chromium steels came into

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use, as well as bimetallic reactors (the outer layer was usually made from chrome-nickel steel and the inner layer from low-carbon steel) [92, 99-103].

It was found that the process could be run at higher temperatures with low-carbon-steel reactors than with stainless-steel designs, since the melting point of the eutectic titanium-iron alloy is 1085°C, and the eutectic alloy of titanium with stainless steel has a melting point of 980-1000°C. As a rule, the titanium crystallizes on the reactor walls and becomes welded to them. If the reactor wall temperature rises above the melting point of the eutectic alloy (titanium-iron), alloying becomes intensive and the reactor wall melts through, air enters the reactor, the titanium sponge reacts with it energetically, the reactor becomes inoperative, and the metal that has been formed is lost to saturation with oxygen and nitrogen.

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In practice, in consideration of the nucleate character of the reduction reactions, as a consequence of which the highest temperature rises suddenly now in one zone of the reactor and then in another, the process is usually conducted at 750-900°C.

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Low-carbon steel, which has a higher eutectic melting point than alloyed steels, also has low resistance to scaling and low stability with respect to titanium tetrachloride at the process temperature; it is also inclined to rapid crystalline-grain growth under rapid thermal cycling, with the result that the impact strength of the steel drops sharply and cracks form in the reactor.

Type 1Kh18N9T chrome-nickel steel is more resistant to scaling and interaction with  $TiCl_4$  vapor at high temperatures than low-carbon steel. However, the eutectic of this steel with titanium melts 90-110°C lower than the eutectic with low-carbon steel. Moreover, the molten magnesium in the reactor readily dissolves nickel, which is a constituent of 1Kh18N9T steel, becomes contaminated with it, and contaminates the titanium sponge. Nevertheless, these steels are widely used in building the reactors.

Types OKh13, Kh25T, and other chromium steels, which are intermediate between low-carbon and chrome-nickel steels as regards the melting point of the eutectic with titanium and have adequate resistance to scaling, are also more stable against reaction with  $TiCl_4$  vapor at high temperature and dissolve to a lesser degree in molten magnesium than the chrome-nickel steels [92, 102]; they are therefore attractive reactor materials.

Bimetals, such as lKh18N9T steel and low-carbon steel, lKh18N9T and Kh25T steels, Kh25T steel and titanium, and others are of great interest for reduction-reactor fabrication. In spite of the greater difficulty of reactor fabrication and the somewhat higher cost of the reactors, use of such steels with inner surfacing of low-carbon steel, Kh25T steel, or titanium makes it possible to raise the productivity of the equipment substantially and improve the quality of the titanium product; in the last analysis, this clearly covers the increased first cost of the reactor [92, 102].

One of two reactor types is usually used under industrial conditions: a reactor with an inserted reaction shell made from one of the above materials or a reactor without such a shell. The reaction shell protects the reactor casing from melting through and permits the use of a stainless-steel reactor and a low-carbon shell; it also facilitates extraction of the reaction mass from the reactor after completion of the reduction process [12, 13, 14, 18, 21]. On the other hand, use of a shell results in formation of a gap between its wall and the reactor wall, to the great detriment of heat transfer out of the reaction zone; it also reduces the useful volume of the reactor and productivity along with it. Furthermore, the machinery used to drain the magnesium chloride becomes more complicated, and lower chlorides of titanium may form in the space between the walls. After each run, the inner surface of such a reactor must be thoroughly cleaned of titanium and magnesium chlorides by washing with hydrochloric acid solution. This operation is time-consuming and injurious to the service personnel, and wears the reactor out more rapidly.

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Reactors without the inserted reaction shell are now in use [99, 100, 105, 106-108]. Use of such reactors becomes especially advantageous when subsequent separation of the magnesium and magnesium chloride from the titanium is undertaken by vacuum separation on the block of reaction mass. The absence of the space between the reactor wall and the reaction mass improves heating of the mass during separation, with the resulting sharp increase in reactor output. Studies made under industrial conditions have shown that conversion from reactors with inserted shells to reactors without the shells raised reduction-furnace and separation productivity by 30-50%, increased the amount of titanium sponge extracted per cycle by 50% as a result of superior utilization of reactor volume, and improved the labor productivity of the servicing personnel by 30% [102].

The disadvantages of the unshelled reactor are the greater danger of melting through the casing and the need for more flexible cooling of the reactor walls in the reduction process in order to avoid freezing of a liner onto these walls, since this would interfere with magnesium transport into the reaction zone.

One of the basic requirements made of a reduction reactor is reliable sealing at high temperatures and the absence of cold zones in its working space, since lower titanium chlorides might form and sublimes might condense in such zones. Reactor sealing must be improved by minimizing the number of weld seams on the casing and use of a reliable cover packing.

Reactor cover and casing flanges are sealed with packings made from highly pure aluminum or annealed copper, which are protected from reaction with titanium chlorides by asbestos [107]. Vacuum rubber is also used in the gaskets; in this case, the cover and casing flanges must be water-cooled.

Great interest attaches to welding of the flanges to seal the reactor; this makes it possible to load the reactor bodily into the furnace, to eliminate cold zones in the working space, to mechanize the time-consuming process of packing and removing the cover, and to obtain more reliable sealing for high temperatures [92, 107, 108, 127]. Use of such a reactor may increase

the process rate sharply, as well as the utilization of  $TiCl_4$  and magnesium.

The reactor cover must be thoroughly heated; variously designed internal screens and external heaters are used for this purpose [102]. In addition, reactors whose covers are sunk down into the reaction zone have recently come into extensive use [128].

The reactor is evacuated and the titanium tetrachloride and argon are fed into it through a central pipe in its cover. The magnesium chloride is drained from the reactor through a siphon that pipes it out onto the service platform through the cover or the side wall of the reactor directly below its flange [107]. In other cases, the magnesium chloride is drained through pipes in the side or bottom center of the reactor, which are sealed with bayonet locks or by freeze-plugging of the drain hole [105, 107].

Figure 39 is a diagram of an industrial unit without a shell insert (with bottom drainage of the magnesium chloride) and an electric reduction furnace.

As we noted earlier, amounts of heat ranging from 100 to 200 thousand kcal per hour are released during the reduction process in modern reactors. It is therefore necessary to have an efficient system for withdrawing heat from the reactor. Solution of this problem may be made easier by holding the zone in which most of the reactions take place at a certain level in the

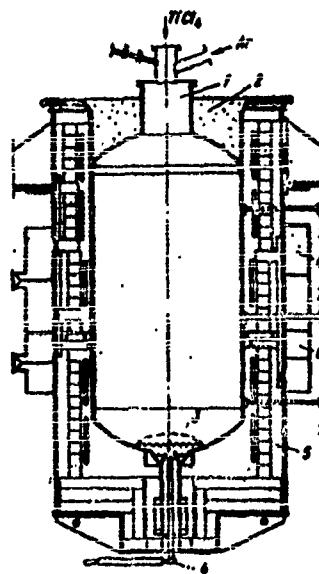


Figure 39. Diagram of electric furnace and reactor for magnesium reduction of titanium tetrachloride. 1) Reactor; 2) cover; 3) perforated floor; 4) shutoff device for drainage of magnesium chloride; 5) electric furnace; 6 and 8) air manifolds for cooling-air supply to furnace; 7) temperature senders.

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reactor. The height of this zone in the reactor can be regulated by holding the melt level in a certain range and regulating the drainage of accumulated magnesium chloride. As a rule, heat is taken from the reactor by cooling the zone of preferential reaction with air supplied to the furnace from a ventilating unit. The cooling air is fed in at several points around the circumference of the furnace, through 2-3 horizontal rows of nozzles. The fans are switched on to deliver cooling air at periodic intervals by an automatic system that signals a temperature rise in one or another zone of the reactor [92, 99, 100, 102-104].

The bottom of the reactor must be heated to support normal reduction when the reaction zone is cooled. Heating is necessary to keep the magnesium chloride liquid in order to facilitate separation of the magnesium and magnesium chloride and smooth delivery of magnesium into the reaction zone; it also facilitates regular drainage of the magnesium chloride from the reactor.

Undercooling of the reactor below the reaction zone retards the delivery of magnesium into this zone and upsets the reduction process, which slows down sharply and yields large quantities of lower titanium chlorides.

To prevent cooling air from entering the bottom zone of the furnace, the furnace has packing rings that separate the cooled and heated zones of the furnace.

Furnaces that are heated electrically and fired with gas and fuel oil are now used as reduction furnaces; they may have several independent heating and cooling zones [102, 105, 107, 123].

Figure 40 shows a reactor 1200-1300 mm in diameter and 1700 mm high; it has no shell insert and is used at the Henderson plant in the USA [92]. Figure 41 shows the titanium-reduction

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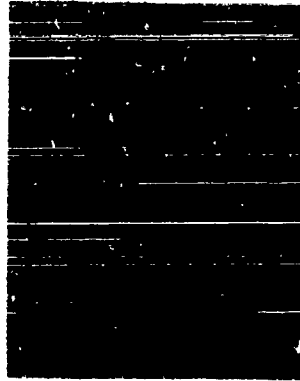


Figure 40. Reactor for magnesium reduction of titanium tetrachloride.

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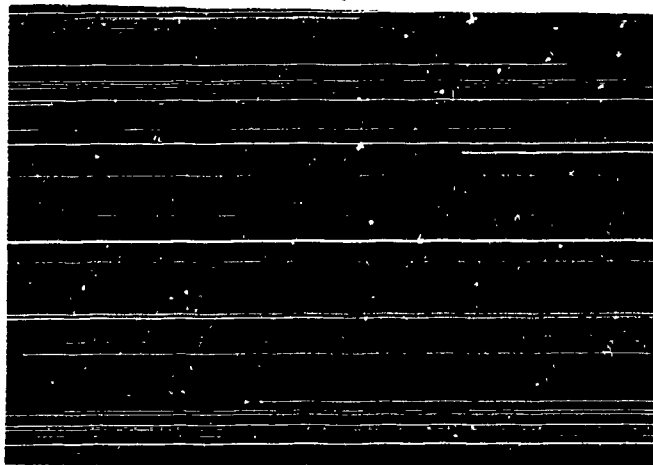


Figure 41. Separation area of process for magnesium reduction of titanium tetrachloride. The  $TiCl_4$  measuring tanks can be seen behind the reduction furnaces.

section at an Asaka Titanium plant (Japan), which uses low-carbon-steel reactors with shell inserts, diameters of 1240 mm, heights of 2600 mm, and wall thicknesses of 50 mm.<sup>(3)</sup> The French plant at LePrese uses reactors 2000 mm high and 1200 mm in diameter, and its reduction furnaces are oil-fired [123].

#### Preparation of Apparatus and Reagents

To prevent contamination of the titanium sponge by gases and moisture adsorbed on the inner walls of the equipment and by oxygen from oxide films and hydrolyzed magnesium chloride, the reaction shell and reactor are thoroughly cleaned before use in the reduction process.

When a reactor with an insert reaction shell is used, the inner surface of the reactor is cleaned mechanically and etched with a dilute hydrochloric acid solution, followed by drying.

If a liner containing magnesium chloride has been left on the walls of the reaction shell after the reaction mass has been cut out on a machine, the shell is treated in what are known as "dry rooms" to prevent hydrolysis; the air humidity in these

Footnote (3) is on page 305.

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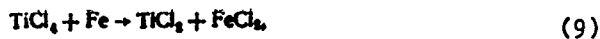
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rooms is held at dew-point level at  $-40^{\circ}\text{C}$ . The shell is charged with magnesium and installed in the reactor under the same conditions, after which the unit is sealed, evacuated, and filled with dried inert gas.

When an unshelled reactor is used and the reaction mass will be purified by vacuum separation of a monolithic block, the reactor walls are coated after removal of the sponge by a titanium lining that provides good corrosion protection for them and protection against iron contamination for the sponge that settles on the reactor walls during the next process. In this case, the inside surface of the reactor is prepared for the process by cleaning with wire brushes (without disturbing the lining) and flushing with compressed gas. As a rule, the sponge liner contains residues of unseparated magnesium chloride and also adsorbes gases and moisture onto its developed surface. For this reason, the reactor must be insulated as quickly as possible from contact with atmospheric air in order to reduce the degree of  $\text{MgCl}_2$  hydrolysis. When such a reactor is dried, measures must be taken to protect the titanium liner from oxidation.

The reactor walls are coated with titanium liner on other areas besides their points of contact with the titanium-sponge block. A layer of titanium sponge also forms on the inner reactor and cover surfaces above melt level. This may result from deposition of minute particles of titanium that has been reduced in the gaseous phase or [107] from reduction of titanium chloride by iron in the reactions



or



At elevated temperatures, the titanium sponge that has formed on the wall surfaces of the reactor welds to the reactor material and forms a dense diffusion layer that protects the steel surface from reaction with  $\text{TiCl}_4$  and from solution in the fused magnesium; this reduces iron contamination of the basic mass of titanium

sponge. The coating of the overheated, oxide-free reactor surface by a titanium layer that results from interaction with  $TiCl_4$  may be used to plate materials with titanium -- a process that advances must efficiently in the presence of hydrogen [107].

The magnesium is loaded into the reactor in the solid state, in the form of pigs and large ingots, or in the molten state. In foreign practice, the reactor is usually charged with solid magnesium in the form of small pigs [5, 18, 21]. In this case, the magnesium is thoroughly cleared of surface oxide films and slag inclusions before loading, by etching the pigs in 0.5-1% hydrochloric acid solution and then washing with clean water. The pig surfaces are carefully inspected after clearing of oxide films, and all inclusions, blisters, and cracks that are found are drilled out and countersunk. Some of the pigs are broken up as a control against the presence of slag inclusions.

To prevent oxidation of the pigs after etching, they are loaded into the reactor as quickly as possible. In certain cases, the etched pigs are processed and loaded into the reactor in "dry rooms" [92].

The process of charging the reactor with solid magnesium is very time-consuming, and utilization of equipment working volume is much lower than when molten magnesium is used. When molten metal is loaded, the productivity of the reduction furnaces is increased, since no furnace time is spent waiting for the magnesium to melt and more favorable conditions are set up for mechanization and automation of the process.

In domestic industrial practice, magnesium is usually loaded in the liquid state into a reactor that has been overheated to 800°C [127]. The magnesium is poured in with a special vacuum batching crucible, which serves for storage, transfer, and pouring of the metal into the reactor under conditions that protect the magnesium from oxidation [169]. Figure 42 illustrates one of the methods of loading a reactor with liquid magnesium [106, page 21]. To prevent oxidation of the magnesium flowing from the batching crucible as it is loaded into the reactor, it is

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continuously bathed with an inert gas, which creates a protective atmosphere around the emerging stream of metal. It takes several minutes to pour the metal. Before it is placed in the pouring crucible, the magnesium is thoroughly refined to remove metallic impurities and suspended matter and to separate it from molten fluxes and electrolyte. In certain cases, the magnesium is filtered through cermet filters, e.g., filters made from the fine fractions of titanium sponge, as it is poured into the reduction reactor [102]. With suitable design of the apparatus and high skill on the part of the servicing personnel, the quality of titanium sponge produced in reactors charged with molten magnesium is higher than when a solid reducer is used.

The reactor, with or without its load of magnesium, is evacuated to 200-400  $\mu\text{m}$  before installation in the furnace and checked for tightness. Sealing is considered adequate if the residual-pressure increase in the reactor (also known as inleakage) does not exceed 5-8  $\mu\text{m}/\text{min}$ .

After testing for tightness, the reactor is filled with dried inert gas (usually argon) and installed in the reduction furnace. To degasify the reactor walls and the surface of the solid magnesium, the reactor is heated to 400°C in the furnace (to 600°C in the case of a reactor without a load of magnesium) with simultaneous evacuation. When the desired temperature has been reached, the reactor is filled with dry argon and heated to 650-760°C, i.e., until all of the magnesium has been melted and slightly overheated. At this temperature, the inert-gas pressure in the reactor is lowered to 0.05-0.10 atm and the reactor is ready for the reduction process.

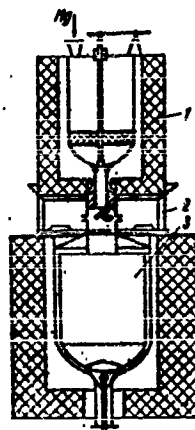


Figure 42. Diagram of installation for charging reduction reactor with molten magnesium. 1) Magnesium batching crucible in constant-temperature jacket; 2) guide frame; 3) reduction reactor.

Highly purified argon is used in the reduction process; before delivery into the reactors, it is usually passed through a vessel filled with titanium sponge that has been heated to 750-900°C to purify it further of oxygen, nitrogen, and moisture [16, 102]. Sometimes helium is used instead of argon to increase heat conduction in the reactor gas space [92, 107]. Here, however, it must be remembered that technical helium is of unsatisfactory purity. Specially purified or spectrally pure helium is incomparably more expensive than argon.

#### Reduction Technology

After all of the magnesium has been melted and its temperature has reached 740-780°C, delivery of titanium tetrachloride into the reactor is started. In occasional cases, the  $TiCl_4$  is fed into the reactor at temperatures of 650-700°C. It is usually supplied through a central pipe fitting on the reactor cover. The  $TiCl_4$  supply to all reducers is either centralized or via individual  $TiCl_4$  batching tanks, one for each unit; in some cases, the  $TiCl_4$  is filtered before delivery into the reactor, usually through ceramic filters [102].

At the start of the reduction process, before  $TiCl_4$  is fed into the reactor, the magnesium surface and the reactor walls are coated with a thin film of oxides, and the magnesium does not wet the passivated reactor walls [107]. As a result, the reduction process will obviously advance very slowly, and for the most part in the gaseous phase, when the first portions of  $TiCl_4$  are fed into the reactor. During this time, the pressure of the vapor-gas mixture often rises to 250-400 mm Hg, so that it is necessary to bleed mixture from the reactor periodically. Temperature is also unstable; the maximum-temperature zone is held above the level of the molten magnesium on the walls and cover of the reactor. The specific  $TiCl_4$  flowrate (the flowrate referred to 1 cm<sup>2</sup> of reactor cross section) is low and does not exceed 6-8 g/(cm<sup>2</sup>·h). During this time, large quantities of lower titanium chlorides form in the reactor; this is because of the deficiency of reducing agent and the elevated  $TiCl_4$  and argon pressures.

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So it continues until particles of reduced titanium appear on the melt surface and the reactor walls. Interacting with the oxide films, the titanium reduces them and de-passivates the surface of the reducing agent and the reactor walls. The magnesium then begins to wet the surfaces of the titanium particles and comes into contact with the titanium tetrachloride on this surface.

As a result of the increased numbers and area of the titanium particles, the rate of the reduction process rises rapidly, the pressure of the vapor-gas mixture drops, and the temperatures in the reactor are levelled out and stabilized. The process enters its main stage. The titanium particles formed during this phase of the reduction process absorb oxygen, nitrogen, and moisture present in the vapor-gas mixture and oxygen from oxide films and impurities in the magnesium. In the normal course of the process, most of these contaminated particles settle at the bottom of the reactor. If reactor-wall temperature decreases, substantial numbers of contaminated titanium particles may be crystallized. If the reactor walls are not undercooled, no substantial amount of sponge forms on them during the initial period of the process.

Extensive practice in the magnesium reduction of  $TiCl_4$  under industrial conditions and specially designed experiments have shown that this complex process can be standardized to a substantial degree and adapted for automatic control. It has been established that the most favorable conditions result when the temperature schedule in the reactor is controlled by programmed variation of the  $TiCl_4$  flowrate with correction of temperature conditions by forced cooling of the reactor [92, 196, 119, 122, 127, 172, 329].

Several schedules have been proposed for standardization of the reduction process; they can be classified for convenience into four types. Schematic diagrams appear in Fig. 43a [329].

I. During the second half of the process, the rate of  $TiCl_4$  supply to the reactor is lowered progressively with the purpose

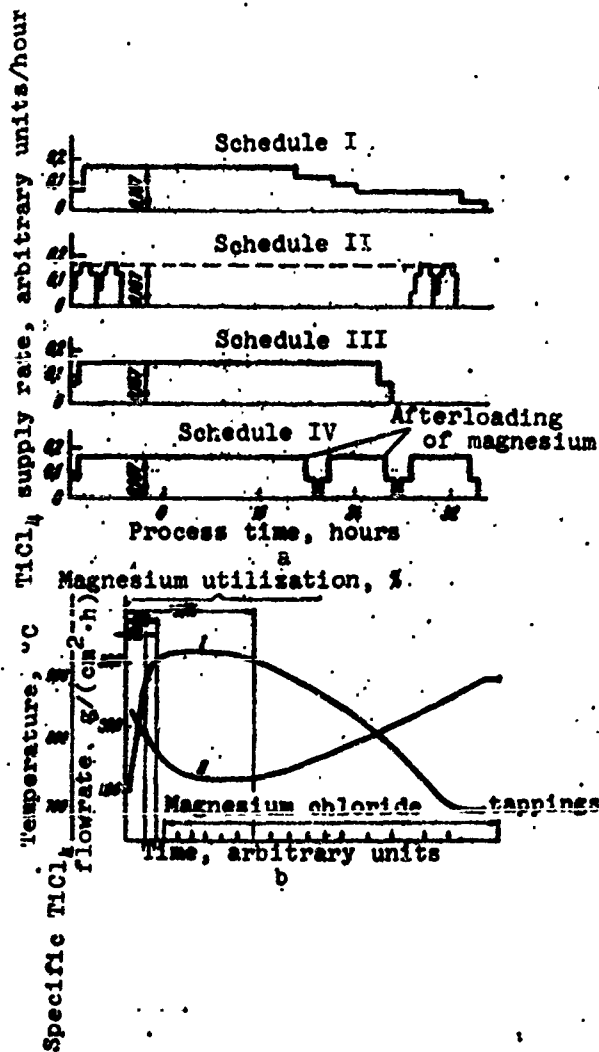


Fig. 43. TiCl<sub>4</sub> reduction conditions. a) Schematic diagram showing stabilization of reduction process; b) variation of specific TiCl<sub>4</sub> flowrate and temperature at reactor wall during programmed reduction process.

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of better reducing-agent utilization.

II. The schedule is based on the assumption that the process is autocatalytic in nature. The rate of  $TiCl_4$  supply to the reactor is varied to conform to the cycles of variation of its partial pressure in the reactor (as a function of the rate of accumulation of  $MgCl_2$  in the reactor).

III. In this type, the maximum possible  $TiCl_4$  flowrate is stabilized throughout the entire process.

IV. This formula differs from the preceding one in that additional quantities of reducing agent are loaded into the reactor in large portions during the process. Conditions are stabilized after each addition, as in the preceding schedule. This schedule makes it possible to increase the per-cycle output of the reactor, chiefly through better utilization of its volume.

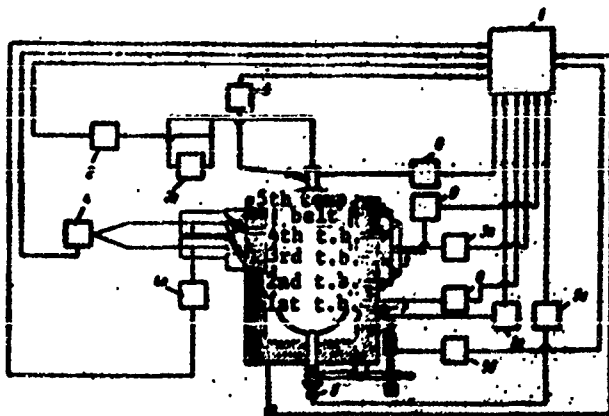


Figure 44. Diagram showing automatic control of reduction process. 1) Programming, control, and annunciator panel; 2)  $TiCl_4$  flowmeter with regulating valve 2a; 3) temperature senders for measurement of temperature in reaction zone with multiposition potentiometer 3a; 4) furnace cooling fan with actuating mechanism operating dampers in air manifold 4a; 5) tension scales with weigher 5a and valve 5b of magnesium chloride drain unit pneumatic drive cylinder; 6) regulating units for argon and titanium tetrachloride pressures in reactor; 7) thermocouple with potentiometer 7a for measurement of temperature in bottom zone of reactor; 8, 9) voltmeters

Below we present the basic indicators of the reduction process for each of the schedules examined above.

|   | I   | II   | III | IV   |
|---|-----|------|-----|------|
| Reactor cycle output, arbitrary units                                     | 1.0 | 1.0  | 1.0 | 1.15 |
| Magnesium utilization factor, %   | 70  | 62   | 62  | 62   |
| Full cycle time, h  | 47  | 44.5 | 39  | 46   |
| Amount of commercial metal obtained per reactor per year, arbitrary units | 186 | 197  | 225 | 219  |

As we see from these data, schedule III is most advantageous. However, schedule IV will evidently be more efficient when equipment that permits loading the reactor with molten magnesium without interrupting the  $TiCl_4$  supply is developed.

Figure 43b presents the standard diagram that was used as a basis for standard reduction processes in industrial reactors at one of the domestic plants. The  $TiCl_4$  flowrate is given in terms of one square centimeter of initial reactor cross section. Temperature is measured with external temperature sensors. Figure 44 is a diagram of automatic reduction-process control in accordance with a preset program. This diagram relates the  $TiCl_4$  flowrate with temperature, cooling-air-fan operation, and furnace heating. The system provides for automatic tapping of the magnesium chloride and maintenance of a given argon pressure in the reactor [127, 170].<sup>(4)</sup> Other automatic-control schemes for the reduction process exist [107, 172].

We see from Fig. 43 that the rate of the process increases rapidly until 10% of the magnesium has been utilized. Even before the first magnesium chloride is drained, the reaction surface increases to the point that the process rate reaches its maximum and remains there as long as there is an excess of magnesium in the reactor and until the rate of its transport into the reaction zone limits the reaction rate. This period of peak efficiency continues until 40-50% magnesium utilization. During this time, the offtake of heat from the reactor is at maximum, so that the lowest reactor wall temperature values correspond to it on the temperature curve. After utilization of the magnesium

Footnote (4) is on page 305.

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has proceeded beyond this limit, the process slows down in spite of the developed reaction surface as a result of the increase in the amount of magnesium in the sponge pores with increasing quantity of reduced titanium. The reduction rate comes to be limited by the magnesium transport rate into the reaction zone. During this time, better conditions for magnesium transport are created at the reactor walls, which are coated with sponge having a developed porous structure. Magnesium passes into the reaction zone through capillaries in this sponge. This is one of the causes of the rapid growth of the lining in the last stage of the process.

At 60-70% magnesium utilization, the conditions are such that all of the unreacted magnesium is in sponge pores, where it can be contacted by the titanium chlorides only with difficulty. This is what determines the maximum degree of magnesium utilization. It has been reported that the magnesium utilization factor reaches 75-85% in some cases [105, 107]. It has also been established that as the rate of the reduction process rises, the pore sizes in the sponge decrease, with the result that active titanium reduction and crystallization centers form in large numbers [100]. Thus, other conditions the same, the general rule is that the higher the rate of the reduction process, the lower the magnesium utilization factor.

It has been proposed that magnesium be loaded into the reactor during the reduction process to improve the utilization factor and reactor useful volume [102, 105, 107]. The afterloaded magnesium may be introduced in solid form with special cartridges and batchers or in the liquid state with equipment similar to that shown in Fig. 42. It is extremely important that the reactor be kept sealed during this process and that no air be admitted to it.

The magnesium chloride drainage schedule is of great importance for normal conduct of the process and formation of sponge. An adequate amount of magnesium chloride in the reactor promotes better layering of the magnesium and facilitates its transport into the reaction zone. Sponge forms and lower titanium chloride

are further reduced in the fused magnesium chloride. At the same time, an excess of magnesium chloride lowers the utilization of reactor useful volume and covers a large reaction area with melt, thus lowering reactor productivity.

Magnesium chloride is usually drained several times during the reduction. Here the tapping schedule is established so as to keep the melt level and the preferred reduction-reaction front in the zone in which the reactor is most effectively cooled. There are equipment designs with continuous magnesium chloride drainage. (5)

As magnesium chloride accumulates in the reactor, an increasingly large reaction area is covered with the fused salt, and the volume of the gas space is reduced. As a result, the process rate gradually falls off, and the pressure of the vapor-gas mixture rises, reaching 150-250 mm Hg before the next tapping of the salt. The former lowers reactor productivity, and the latter creates conditions favoring the formation of lower titanium chlorides.

Drainage of magnesium chloride exposes magnesium-wetted sponge surface, with the result that the rate of reaction with the reducing agent increases and the vapor-gas pressure drops to a few mm Hg.

Cases have been observed in which the temperature rose abruptly in one of the reactor zones after the magnesium chloride was tapped. This is obviously to be explained by further reduction of lower titanium chlorides by magnesium brought down when the salt was drained (for the most part, further reduction of  $TiCl_2$ , which crystallizes out of the salt in certain undercooled zones).

The temperature in the reactor is the principal factor in determining the type of reaction between the  $TiCl_4$  and the magnesium, the sponge-forming process, reactor productivity, and sponge quality. Temperature cannot be measured at the center of the reactor, in the reaction core, since there are no thermocouple-jacket materials that are stable in  $TiCl_4$  at temperature above 1000-1200°C. At any rate, temperature measurement at the walls of the reactor rather than at the center is of greater

Footnote (5) is on page 305.

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interest for industrial practice. This temperature must be known in order to prevent the melting of holes in the reactor wall or freezing of the reaction mass onto the walls. These measurements are sometimes made with a multifunction thermocouple in a protective jacket mounted on the inner wall of the reactor. Then, however, the jacket shields the thermocouple and prevents accurate measurement of reactor wall temperature. Focal reduction reactions often develop on the jacket, and this also distorts data on the temperature conditions in the wall layer of the reactor. In addition, the installation of internal thermocouples complicates the design of the equipment and the subsequent extraction of the reaction mass or sponge. For these reasons, internal thermocouples have recently been supplanted increasingly with temperature senders with which the temperature on the reactor outer wall is measured.

As we see from Fig. 43, the temperature in the wall layer of the reactor is held at a level determined by the  $TiCl_4$  flowrate specified for the particular phase of the process. For this purpose, the  $TiCl_4$  flowrate and the on-off switching of the fan that supplies cooling air to the reactor outer surface are controlled automatically.

Cooling of the reactor below the optimum temperatures results in the formation of large amounts of lower titanium chlorides and upsets the reduction process. Cases have been observed in which low temperatures and  $TiCl_4$  flowrates have caused much of the reduced titanium to crystallize on the reactor walls and gradually cover its entire cross section -- the formation of a so-called "bridge," accompanied by a sharp deceleration of the reduction process, since the supply of magnesium to the reaction zone stops and it is difficult for the  $TiCl_4$  to make contact with the reducer.

At above-optimum temperatures, conditions are created for vaporization of the magnesium and the gaseous-phase reactions. This results in the formation of a large amount of dispersed, pyrophoric titanium, which makes the subsequent operations of extracting the sponge from the reactor and gridding it much more

difficult and also reduces the amount of high-grade titanium extracted from the  $TiCl_4$ . Moreover, the reactor material interacts more vigorously at elevated temperatures with the reagents present in the reactor, to the detriment of titanium quality. Elevation of the temperature may cause the reactor to melt through and, consequently, a breakdown in which expensive titanium sponge is spoiled. Under normal process conditions, the optimum reactor outer wall temperature is held in the 750-850°C range. The temperature in the bottom zone of the reactor is usually about 750°C, since this supports better tapping of the magnesium chloride [92].

At the end of the reduction process, when the supply of  $TiCl_4$  has been shut off to permit further reduction of lower titanium chlorides and more complete separation of the magnesium chloride, there is a 30-60-minute hold at 900°C, after which the last magnesium chloride is tapped.

After the high-temperature hold, argon is admitted to the unit and it is cooled in the furnace to 800°C (in the case of a stainless-steel reactor) or 600°C (in the case of a low-carbon-steel reactor) to protect the reactor outer surface from severe scaling resulting from exposure to air. Subsequent cooling of the unit to 20-40°C takes place on a special bench, on which its surface is sprayed with water or flushed with air.

#### Certain Variations of the Periodic Process

One version of the magnesiothermic process proposes the use of magnesium condensate as a reducing agent for titanium tetrachloride; this material is obtained on removal of the magnesium chloride and magnesium from the reaction mass during vacuum separation [155, 158]. Here the magnesium and magnesium chloride sublimates are condensed directly in the reduction reactor during the process of vacuum separation [115]. On completion of vacuum separation and cooling of the condenser-reactor under conditions that minimize contact between it and atmospheric air, the reactor is dismantled, covered, sealed, evacuated, filled with dry inert gas, and installed in a reduction furnace. The tetrachloride can be supplied into a reactor with magnesium condensate

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starting at temperatures as low as 250-400°C, since dispersed magnesium is highly active at this temperature and reacts vigorously with  $TiCl_4$ . After the temperature has risen to 700-800°C and all of the condensate has melted, the process is similar to the conventional reduction. This process makes it possible to increase equipment productivity, since the warmup time before  $TiCl_4$  supply begins is shorter (going to 250-400°C rather than the usual 740-780°C). The process of remelting the condensate in special furnaces is also eliminated, and this lowers operating costs and reduces magnesium losses. The quality of the resulting titanium sponge depends strongly in this case on the effectiveness with which oxidation of the condensed, dispersed magnesium and moistening of the magnesium chloride can be prevented during the period in which they are in contact with ambient air (when the unit is disassembled after termination of the reduction process, and during its assembly for vacuum separation).

With a view to lowering the temperature of the process, attempts have been made to reduce  $TiCl_4$  to obtain a low-melting salt melt. A mixture of magnesium and sodium was used as a reducing agent for this purpose, or sodium, potassium, and other chlorides were injected into the reactor [103-105, 107]. However, this did not markedly improve magnesium utilization, processing of the reaction mass was complicated, and the grain size and quality of the sponge deteriorated.

Numerous attempts have been made to supply the titanium tetrachloride to the unit simultaneously with molten or gaseous magnesium with the object of increasing reactor productivity and magnesium utilization. Thus, several patents propose that the  $TiCl_4$  and magnesium be introduced into the reactor gas space with special tangential and swirl-type nozzle injectors.<sup>(6)</sup> Other patents suggest introduction of magnesium into a bath of fused magnesium chloride or batched injection of magnesium vapor into a chamber containing  $TiCl_4$  vapor by means of a special distribution tank.<sup>(7)</sup> Another method envisages simultaneous injection of  $TiCl_4$  vapor and magnesium powder into a reactor that has been preheated to high temperature.<sup>(8)</sup> However, a major obstacle to the

Footnotes (6), (7) and (8) are on page 305.

implementation of these processes is the absence of sufficiently reliable flow-control and batching equipment for molten and vaporized magnesium; another is the fact that when  $TiCl_4$  and magnesium are supplied simultaneously to the reactor, the  $TiCl_4$  and magnesium feeders are quickly overgrown by titanium sponge. Moreover, these methods usually produce large amounts of dispersed, pyrophoric sponge, and this makes its processing difficult and lowers the grade of the metal.

Holst and Proft proposed a method for reduction of  $TiCl_4$  with magnesium vapor in a vacuum rather than in the usual inert-gas atmosphere [151]. Here, both processes (both the reduction of  $TiCl_4$  and separation of the reaction mass obtained after reduction) are carried out in the same apparatus. The apparatus is a reduction reactor with a top-mounted water-cooled condenser. Magnesium pigs are loaded into the reactor, which is then sealed and evacuated to 60-70 mm Hg, with simultaneous preheating to 700°C. When these conditions have been reached,  $TiCl_4$  vapor is admitted to the reaction space above the pig magnesium and reacts with the sublimated magnesium vapor. During the reduction reaction, the condenser gas space is disconnected from the reaction-chamber space, and the process takes place in the bottom of the unit, where the titanium and magnesium chloride form and the unreacted magnesium remains.

When the  $TiCl_4$  supply has been shut off, the unit is evacuated with simultaneous heating to 900-1000°C. Communications is then opened between the reaction chamber and the condenser, where the magnesium chloride vapor condenses and the magnesium drains in the molten state into a special receiver. The titanium sponge left in the reactor contains, on the whole, from 0.1 to 0.5% magnesium chloride and manganese, and the extraction of titanium into the commercial sponge is 85-90%. The shortcomings of this method consist in the formation of a fine sponge, lower  $TiCl_4$  utilization owing to the formation of lower titanium chlorides in considerable amounts, and the impossibility of periodic tapping of the magnesium chloride product while maintaining a high vacuum in the reactor. This last circumstance sharply reduces reactor

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productivity, which does not exceed 100 kg of titanium sponge per cycle. Other design versions of the equipment for this process have been submitted [152], but they are all host to the above shortcomings.

#### Vacuum Separation of Reaction Mass

The reaction mass obtained as a result of magnesium reduction of  $TiCl_4$  contains about 50-70% of titanium sponge, 30-35% magnesium, and 15-20% magnesium chloride. The maximum permissible chlorine and magnesium contents in refined commercial sponge may not exceed 0.08-0.12% and 0.1-0.5%, respectively.

The reaction mass can be separated by either of two fundamentally different methods: sublimation of the magnesium chloride and magnesium in a vacuum at high temperatures, or leaching of the reaction mass in 0.5-1.0% hydrochloric acid.

Sublimation of magnesium chloride and magnesium from the reaction mass in vacuum separation is based on the large difference between the vapor pressures of the reaction-mass components at high temperature. As we see from Table 30, magnesium can be distilled out of the reaction mass at a temperature above its boiling point (1103°C), and the magnesium chloride at a temperature above its boiling point (1418°C). At these temperatures, however, titanium sponge reacts vigorously with the reactor materials, with the result that sponge quality deteriorates sharply. Furthermore, it is impossible to remove the magnesium chloride and magnesium from the sponge thoroughly enough under these conditions.

It has been suggested that the process be conducted under a hard vacuum with the purpose of lowering the temperature and removing more of the magnesium chloride and magnesium from the reaction mass [103-106].

At a residual pressure of about 50  $\mu$ m Hg, the boiling point of magnesium chloride is approximately 700°C, and that of magnesium about 400°C. However, these are the figures for magnesium and magnesium chloride in the free state. In the reaction mass, the magnesium chloride and magnesium occupy pores in the titanium

Graphic Not Reproducible



Figure 45. Machine for drilling reaction mass out of reduction reactor.

sponge, including extremely fine pores deep in its interior. Hence to accelerate the process and obtain more complete sublimation, vacuum separation is usually carried out at 950-1000°C [92, 107, 158].

The reaction mass may be subjected to vacuum separation in the form of a monolithic block or in the form of chips. In the latter case, the reaction mass is cut out of the reactor on a special machine (Fig. 45) after completion of the reduction process and cooling of the reactor. To prevent moistening of the hygroscopic magnesium chloride, the reaction mass is machined out in special so-called "dry rooms," where the air humidity corresponds to dew points at -26 to -50°C [106, 107, 159, 167]. Vacuum separation of chips permits more efficient utilization of separator volume and facilitates the subsequent operation of removing the sponge from the reactor. However, even in rooms with air humidities below 0.5 g/m<sup>3</sup>, magnesium chloride takes up appreciable amounts of moisture during the machining-out process; a contributing factor here is the increased contact area between the magnesium chloride and atmospheric moisture when the chips are cut. In addition, the chips are more strongly heated than a monolithic block under a hard vacuum, and this increases the time required for the process. The construction and operation of "dry rooms" complicate the technological process and raise the cost of the

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Proposed methods for cutting out the reaction mass in a vacuum [106, page 27] have not come into industrial use because of their complexity.

In industrial practice, the preferred method is separation of a monolithic reaction mass [92, 197, 158, 167]. Here it is easier to avoid appreciable moistening of the reaction mass, but somewhat more difficult to drive the magnesium chloride out of the depths of the block; it is also harder to remove the separated sponge from the reactor [107, 158, 168].

Figure 46 shows a diagram of a vacuum-separator installation [172], and Fig. 47 a general view of a vacuum-separation section.

A balancing vacuum (10-50 mm Hg) is set up in the furnace to reduce the load on the reactor casing with its load of reaction mass at 900-1000°C, which is evacuated to a residual pressure of a few microns, and to prevent air from entering the reactor.

The assembled unit is carefully sealed and checked for tightness. The vacuum loss in the assembled cold unit after evacuation to a residual pressure of 50-60  $\mu\text{m Hg}$  may not exceed 1-2  $\mu\text{m Hg}$  per minute. After checking for tightness, the unit is pumped out to a residual pressure below 0.2 mm Hg and the furnace to 10-50 mm Hg; the electric heating is then switched on and the

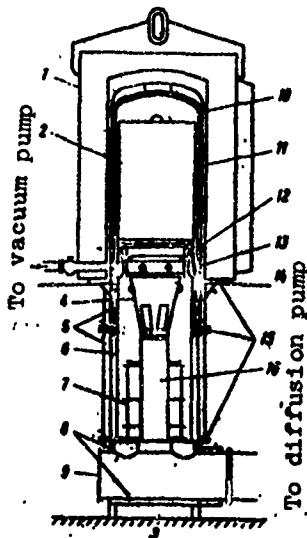


Figure 46. Diagram of apparatus for vacuum-thermal purification of titanium sponge. 1) Electric furnace; 2) titanium-sponge block; 3) 1st-stage floor; 4) lower funnel; 5, 8) water-cooling jackets; 6) inner casing; 7) shield; 9) trap; 10) upper retort; 11) inner shell; 12) upper funnel; 13) supporting funnel; 14) upper-platform floor; 15) packing; 16) supporting column.

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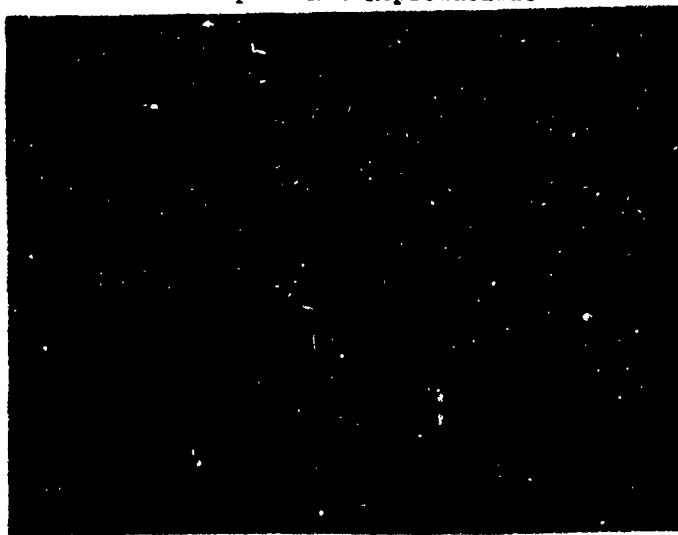


Figure 47. Work area in vacuum-separation department.

reactor temperature is raised while it is pumped [92, 107, 158].

When the temperature has risen to 300-350°C, most of the moisture present in the moist magnesium chloride or adsorbed on the reactor's internal walls has been removed from the reaction mass. Below 300-350°C, the moisture released does not oxidize the titanium sponge, which is coated by a layer of magnesium chloride and magnesium. The rest of the moisture is eliminated as the temperature rises from 500 to 550°C. Above 480°C, all of the moisture released interacts with the titanium sponge, contaminating it with oxygen and hydrogen [65, page 92]. In addition, hydrogen chloride may be released from the reaction mass at 182°C as a result of hydrolysis of magnesium chloride crystal hydrates and formation of MgOHCl. If the reaction mass contains lower chlorides of titanium,  $TiCl_4$  may also be liberated as a result of their disproportionation.

When the temperature in the reactor has been raised above 600-700°C and the residual pressure is below 1 mm Hg, the

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magnesium and magnesium chloride begin to distill violently, with the result that the vacuum in the unit drops and the condenser temperature rises sharply. During this time, the furnace electric heating system is switched off periodically to prevent overheating of the condenser and obstruction of the vacuum system by sublimates. After as little as 8-12 hours have elapsed from the start of vigorous sublimation, most of the magnesium and magnesium chloride have been driven out of the sponge. The residual pressure in the unit then begins a rapid drop. During this time, the temperature may be raised to 960-1000°C. This begins high-temperature holding, during which residues of magnesium chloride are removed from the sponge as the reactor residual pressure gradually descends to 10-20  $\mu\text{m}$ . During this period, which represents about 80% of the total process time, the rate of magnesium chloride and magnesium sublimation is determined chiefly by the rate at which their vapors diffuse out of the depths of the sponge to the evaporation surface [107, 158].

A variety of methods are currently in use for determination of the end of separation. The process is usually broken off after a predetermined high-temperature-holding time and a given stable residual-pressure level in the reactor. This is sometimes supplemented by determination of the vacuum loss in the reactor when it is disconnected from the vacuum system, which should not exceed 1-2  $\mu\text{m}/\text{min}$ . It has also been proposed that the end of the separation process be determined from the temperature of the gas stream,<sup>(9)</sup> or by measuring the residual pressure near the evaporation surface of the magnesium chloride. For obvious reasons, the latter method is more promising.

Under industrial conditions, determination of the end of separation is complicated by the fact that the composition, porosity, pore sizes, etc., of the reaction mass vary substantially from process to process. It is therefore important that the reduction be carried out under standard conditions, which make it possible to produce reaction masses of uniform composition and structure.

When it has been determined that vacuum separation is complete, furnace electric heat is switched off, the reactor is

Footnote (9) is on page 305.

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filled with argon, and, simultaneously, the countervacuum in the furnace is lowered. After the unit has been cooled to the ambient air temperature with the sponge inside it, it is disassembled. The reactor is sent with the sponge to the sponge-refining department, and the condenser to the condensate-remelting department. The magnesium melted out of the condensate is recycled to the reduction process, and the magnesium chloride is sent for electrolysis to recover chlorine and magnesium, which are also recycled.

The completeness with which the magnesium and magnesium chloride are eliminated from the sponge is determined principally by such factors as the high-temperature holding time, temperature, the hardness of the vacuum, and sponge structure [107, 158]. It has also been established that increasing the holding time (for example, from 24-30 to 48 hours) cannot, by itself, lower the sponge chloride content [158]. At the same time, a substantial increase in vacuum-separation time is generally detrimental to sponge quality owing to the reaction between the sponge and air that seeps into the reactor.

Nor does the residual pressure in the reactor at the end of the process determine the completeness of sublimation. Thus, it has been found that when the residual pressure in the reactor is varied from  $2 \cdot 10^{-4}$  to  $2 \cdot 10^{-5}$  mm Hg and other factors are held constant, there is practically no change in the chlorine content of the titanium sponge [108, 158].

The temperature in the reactor has a strong influence on the depth and speed of sublimation. Thus, the magnesium-sublimation rate is doubled when the temperature is raised from 900 to 925°C, but magnesium chloride is removed somewhat more slowly [108, 158].

It has also been established that the lower the porosity and the smaller the size of the pores in the sponge, the more difficult does it become to remove the magnesium and magnesium chloride from it. For example, for the reasons examined above, an increase in the rate of the reduction process reduces sponge porosity and pore dimensions, so that it becomes more difficult to remove

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residues of magnesium and magnesium chloride from the sponge in the separation process. On a slight increase in  $TiCl_4$  feed rate into the reactor, sponge porosity increases from 40-8 to 46.3% [331, 332].

All of the above attests to the fact that in defining conditions for conduct and culmination of the vacuum-separation process it is necessary to consider many factors in order to obtain high-grade titanium sponge.

Separators with bottom- and top-mounted condensers are used in industry. It has been reported that the separation time is shorter in the former case, since some of the magnesium and some of the chloride are melted out of the reaction mass and drain into the condenser; in this case, the condensate is denser and can be remelted easily and with less loss of magnesium [106, page 80]. This creates more favorable conditions for protection of the titanium sponge from contamination by trickling condensate. At the same time, the construction of the removable electric vacuum furnace and condenser used in bottom-condenser equipment is much more complex than in units with top-mounted condensers.

Mechanical sleeve-type and other vacuum pumps, including twin-rotor pumps, are used to evacuate the reactor to a residual pressure of 1-2 mm Hg during the separation process. Multistage oil-diffusion pumps are used to create the hard vacuum. To protect the vacuum pumps from entry of sublimates, the vacuum system is fitted with a number of mechanical and oil filters. As we indicated above, water vapor, hydrogen chloride, and titanium tetrachloride may enter the vacuum system in addition to the magnesium and magnesium chloride sublimates. To protect the vacuum system and pumps from these aggressive substances and to improve the vacuum in the system, it is equipped with special traps holding activated charcoal, alkali heated to 800°C, titanium sponge, or silica gel, or perhaps even with liquid-nitrogen freeze-out traps [106, 167].

To prevent air and vacuum-oil vapor from entering the unit in the event of unexpected vacuum-pump shutdown, the vacuum systems are provided with automatic shutoff valves. <sup>(10)</sup>

Footnote (10) is on page 305.

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Temperatures in the reactor and condenser are usually measured with surface temperature sensors and regulated automatically in accordance with a predetermined program.

The residual pressure in the unit is measured with type VIT thermocouple vacuum gauges.

The vacuum-separation process has important shortcomings, chief among which are:

- a) the intermittent nature of the process;
- b) the low productivity of the equipment, its complexity and high cost;
- c) high electric power consumption (6-10 kW·h per kg of titanium).

A proposal whose object is to increase vacuum-separation-equipment productivity is the combined process considered in Chapter 12, in which vacuum separation is linked with a hydrometallurgical final phase of the process in which residual magnesium chloride and magnesium are driven out of the sponge.<sup>(11)</sup> A number of modifications of vacuum separation in continuous-flow equipment have been suggested,<sup>(12)</sup> as well as variations in which the reaction mass is remelted to dense titanium without removal of magnesium chloride and magnesium from the sponge [65, 161].<sup>(13)</sup> However, these methods have not come into industrial use because of inefficiency or the complexity of equipment design.

From the standpoint of increasing reduction and vacuum-separation equipment productivity, interest attaches to a single unit of equipment that handles both of these processes [162].<sup>(14)</sup> One version of this equipment is a reduction reactor over which a condenser is mounted; during reduction, the reactor working space is hermetically separated from the condenser working space by a special screen with a central plugged hole large enough in diameter to pass the magnesium and magnesium chloride vapors during vacuum separation. When reduction is complete, the condenser working space is evacuated and the hole is unplugged. Since the reaction mass has been heated to about 900°C, the magnesium

Footnotes (11), (12), (13) and (14) are on pages 305 and 306.

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chloride and magnesium begin to sublime off vigorously and condense at the top of the unit, in the condenser.

Here, equipment productivity is increased by elimination of the times required to cool the reactor to 40-60°C after completion of reduction and heat it from 40-60 to 900°C during vacuum separation, as well as elimination of the intervening disassembly and reassembly of the unit between the reduction and vacuum-separation processes.

The essential shortcomings of the combined apparatus:

the impossibility of checking it for vacuum-tightness between the reduction and separation processes;

the relatively complex design;

the extremely violent sublimation of the magnesium chloride and magnesium during the initial separation phase, which makes it necessary to cool the reaction mass after reduction to 300-500°C in order to avoid overheating of the condenser and obstruction of the vacuum system by sublimates.

#### Extraction of Titanium Sponge from Reactor and Processing of Sponge

The titanium sponge that forms in the reactor is strongly welded to its walls. The effort that must be applied to separate the sponge from the reactor material is about 40-100 kg per centimeter of cutting perimeter. The liner part of the sponge is most tenaciously welded to the walls. It is easier to separate titanium sponge from stainless-steel reactor walls than from ordinary steel, since a layer composed of an intermediate alloy of titanium with the stainless steel forms between the sponge and the reactor material and is easier to separate from the reactor walls. When titanium is used as the reactor inner lining, the sponge welds to it so strongly that it is practically impossible to remove it from the reactor walls.

Jackhammers are usually used to separate the sponge liner from the reactor walls and extract the block of titanium sponge after vacuum separation has been completed and the reactor has

cooled. Then the central bloom part of the metal is cut out and the sponge block is extracted from the reactor.

Extraction of the sponge from the reactor by this method is an extremely strenuous and time-consuming operation. However, mechanical methods of cutting the titanium sponge out of the reactor have not yet come into extensive industrial use owing to the severe oxidation suffered by the titanium sponge during cutting. Attempts to prevent sponge oxidation by feeding an inert gas into the cutting zone have not produced the desired results. This is partly because the pores in the sponge itself contain enough air to oxidize the metal vigorously and partly because a substantial amount of moisture is adsorbed on the sponge surface.

Use of cut reaction mass (chips) in vacuum separation is of interest from the standpoint of convenience and ease in extracting the sponge from the reactor. However, as we noted previously, the use of cut reaction mass lengthens the vacuum-separation time and is detrimental to titanium-sponge quality.

In industrial tests, the titanium-sponge blocks were pressed out of the reactor on a 320-ton press. A massive false bottom was placed on the floor of the reactor for this purpose. The press rod passed through the magnesium chloride drain hole of the reactor and bore on the false bottom, which pressed the block out. The sponge can be removed from 3-4 reactors in an hour by this method [316].

At one of the titanium plants of Osaka Titanium in Japan, removal of the sponge is made easier by fitting the reactor with a perforated-bottom shell made from low-carbon steel about 3 mm thick.<sup>(15)</sup> On completion of vacuum separation, the titanium sponge, which has welded itself to the shell, is extracted from the reactor with the shell; the reactor is then cut up and removed from the titanium block, which is cleaned of impurity-contaminated surface films (Fig. 48).

After extraction from the reactor and cleaning, the block of titanium sponge is sent for trimming. First the bottom of the block, the liner, and the surface films, which contain large

Footnote (15) is on a page 306.  
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amounts of impurities and are processed separately from the main block, are removed from it.

The main sponge block, the bloom, is crushed into coarse fragments. Mechanical or hydraulic presses rated at 1-2 thousand tons are usually used for this process. Presses equipped with devices for squeezing rather than cutting the block are preferred, since this minimizes oxidation of the sponge. Presses designed for crushing sponge must eliminate entry of oil, water, and scale into the sponge, and this makes bottom-drive presses more desirable. Moreover, the mechanical part of the press must be protected from entry of titanium dust and be explosion proof.

The sponge is then ground down further, usually in a system of jaw-crusher mills, followed by screening into fractions. Usually, the fractions smaller than 2.0 mm from the main block and the fraction smaller than 6-12 mm from the bottom and lining are screened out and discarded. The maximum size of the titanium-sponge fragments in commercial consignments normally ranges from 12 to 70 mm. Naturally, the finer the sponge, the more uniform will be the composition of the metal in the commercial consignment, but the more finely the sponge is ground, the greater will be the danger of oxidation of the sponge and inferior sponge quality.

After the sponge has been ground and the quality of the metal obtained from the various reactors has been checked, batches of

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Figure 48. Extraction of titanium sponge from reactor and cleaning of bloom. a) Shell with sponge, after extraction from reactor; b) separation of shell from sponge; c) removal of contaminated surface films from bloom.

metal that are most similar as regards chemical and granulometric composition and mechanical properties are combined to form commercial consignments weighing to 5-8 tons. Each charge is thoroughly mixed with any of a variety of mixer types that ensure rapid blending and do not contaminate the sponge with mixer material. One of the mixtures used at an Osaka Titanium plant in Japan is shown in Fig. 49.<sup>(16)</sup>

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Figure 49. Sponge-processing department. In the foreground, containers for storage and transport of the sponge. In the background, a sponge mixer.

After blending, a general sample is taken from the consignment by quartering or automatic intersection. The sample is analyzed chemically and tested mechanically.

The final titanium sponge is placed in sealed containers, in which it is stored and shipped to consumers. Airtightness of the containers is very important, and the container material must have sufficient resistance to rubbing by the titanium sponge during shipment.

Footnote (16) is on page 306.

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Figure 50. Containers for storage and transport of sponge.

Sometimes the containers are evacuated after filling with sponge and then filled with dried inert gas. These precautions are sometimes necessary for long-term storage of the sponge in order to prevent moistening of magnesium chloride residues present in it.

Two containers made from high-strength aluminum alloy and capable of holding 1 to 2.5 tons of titanium sponge are used extensively in American practice for storage and shipment of the sponge [18, 107, 108]. These containers are vacuum-tight, conveniently loaded and unloaded, and can be stored on outdoor platforms (Fig. 50). The containers used at the Osaka Titanium plant are cylindrical, made from galvanized iron, and capable of holding about 200 liters (see Fig. 49). After filling with sponge, the bottom, which has an elastic gasket, is crimped and the container with the sponge is evacuated through a special fitting and then filled with dry inert gas.<sup>(17)</sup> To prevent the sponge from

Footnote (17) is on page 306.

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interacting with the container material, a polymer film is bonded onto the container inner surface and the sponge is enclosed in a liner of the same film inside the container.

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#### Footnotes

- | Manu-<br>script<br>Page<br>No. |   |
|--------------------------------|---|
| 252                            | <sup>1</sup> Also, Patent (USA), No. 2,205,854, 1940.   |
| 262                            | <sup>2</sup> R.A. Sandler, Author's abstract of dissertation, Lenin-grad, 1961.   |
| 276                            | <sup>3</sup> Osaka Titanium brochure, 1960.   |
| 284                            | <sup>4</sup> Timchenko, V.S. et al. Author's certificate (USSR), No. 135,645, 1961.   |
| 286                            | <sup>5</sup> S.N. Sergiyenko and I.P. Maslennikov, Author's certifi-<br>cate (USSR), No. 125,384, 1960.                             |
| 289                            | <sup>6</sup> Patent (Japanese), No. 7808, 1956; Patent (USA), No.<br>2,782,118, 1 57; Patent (West German), No. 1,030,995,<br>1958. |
| 289                            | <sup>7</sup> Patent (Japanese), No. 13,656, 1960; Patent (USA), No.<br>2,772,415, 1956.   |
| 289                            | <sup>8</sup> Patent (USA), No. 2,708,158, 1955.   |
| 295                            | <sup>9</sup> Ustinov, V.K. et al., Author's certificate (USSR), No.<br>132,824, 1960.   |
| 297                            | <sup>10</sup> Author's certificate (USSR), No. 129,907, 1960.   |
| 298                            | <sup>11</sup> Patent (USA), No. 2,933,600, 1961.  |
| 298                            | <sup>12</sup> Patent (Japanese), No. 15,664, 1960; Patent (USA), No.<br>2,778,726, 1957.  |
| 298                            | <sup>13</sup> Also Patent (USA), No. 2,876,064, 1959; Patent (USA),<br>No. 2,817,585, 1959.   |

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298 <sup>14</sup>Patent (Brit.), No. 768.124, 1957; Patent (Japanese),  
No. 8254, 1956; Author's certificate (USSR), No. 125,083,  
1958.

300 <sup>15</sup>Osaka Titanium brochure, 1960.

302 <sup>16</sup>Osaka Titanium brochure, 1960.

303 <sup>17</sup>Osaka Titanium brochure, 1960.

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Symbol List

| Manu-<br>script<br>Page<br>No. | Russian | When<br>Typed | Meaning     |
|--------------------------------|---------|---------------|-------------|
| 255                            | кип     | b             | boiling     |
| 255                            | пл      | m             | melting     |
| 255                            | возг    | sub           | sublimation |

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## Chapter 14

### QUALITY OF MAGNESIOTHERMIC TITANIUM SPONGE

#### General Information

Recent years have witnessed the introduction of titanium into new branches of engineering, including, primarily, rocketry, shipbuilding, and the chemical industry. New refractory and heat-hardenable titanium-based alloys have been developed and put into production to meet the needs of these branches. As a result, the demands made of the titanium sponge as regards purity have risen sharply; this applies primarily to its content of gaseous impurities — oxygen, nitrogen, and hydrogen.

It has been established that for many alloys, increases in hydrogen and oxygen contents lower thermal stability and are quite detrimental to plasticity [175, page 29]. The cold-cracking resistance of joints welded in titanium alloys is lowered substantially when hydrogen content increases [175, pages 24 and 32]. Here, although high hydrogen content is the basic cause of cold cracking in the welded joints, nitrogen and oxygen also contribute to the formation and development of cold cracks by lowering the plasticity of the seam.

In view of the harmful effects of gaseous impurities on the properties of the alloys, rigid upper-limit standards have been introduced for their gaseous-impurity contents. For hydrogen, these limits range from 0.005 to 0.015%, for oxygen from 0.02 to

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0.20%, and for nitrogen from 0.01 to 0.05% [175].

Rigid specifications as to the purity of the metal confront sponge-titanium producers with the problem of lowering the metal's impurity contents significantly. In view of the contemporary trend toward expansion of the titanium industry and the use of titanium in engineering, as well as the need to use titanium scrap in the alloy after machining, it can be stated with confidence that the purity requirements made of titanium sponge will increase steadily in the future, especially as regards its content of gaseous impurities.

The quality of titanium sponge is determined by the following basic characteristics: chemical composition and related mechanical properties; the homogeneity of the metal, i.e., the uniformity of impurity distribution and mechanical properties throughout the entire volume of the commercial lot; absence of oxidized fragments and fragments with chemical composition differing sharply from the basic mass in the commercial consignment.

The purest titanium, which is now produced by the iodide method, contains less than 0.01% O<sub>2</sub>, about 0.002% N<sub>2</sub>, less than 0.02% Fe, less than 0.03% each of C, Al, and Si, and traces of hydrogen, magnesium, calcium, and nickel. Such titanium has a hardness of about 50 HB.

Under industrial conditions, titanium sponge produced by the magnesiothermic method usually contains 0.03-0.15% O<sub>2</sub>, 0.01-0.04% N<sub>2</sub>, 0.02-0.15% Fe, about 0.002-0.005% H<sub>2</sub>, 0.02-0.12% Cl, 0.01-0.05% Si, 0.01-0.03% C, about 0.01% Al, 0.01% Ni, 0.01% , and other impurities. The hardness of magnesiothermic sponge varies from 90-100 to 160-180 HB, and in some cases to 200-220 HB.

Table 32 lists chemical-composition and hardness requirements for titanium sponge produced in various countries.

Owing to the complexity and chiefly to the imprecision of existing methods for quantitative impurity determination (especially for oxygen), determination of mechanical properties has been introduced into the technical specifications for sponge titanium to supplement determination of its chemical composition. Here

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**TABLE**  
**Technical Specifications for Titanium Sponge Produced**

| Type of titanium sponge        | Designation | Mechanical properties |                                  | Chemical |           |           |
|--------------------------------|-------------|-----------------------|----------------------------------|----------|-----------|-----------|
|                                |             | HB, max.              | $\sigma_s$ , kgf/cm <sup>2</sup> | Ti, %    | N, %      | C, %      |
| USSR                           |             |                       |                                  |          |           |           |
| Separated magnesiothermic      | TG108       | 100                   | —                                | —        | 0.02      | 0.03      |
|                                | TG110       | 110                   | —                                | —        | 0.03      | 0.03      |
|                                | TG120       | 120                   | —                                | —        | 0.03      | 0.04      |
|                                | TG130       | 120                   | —                                | —        | 0.03      | 0.04      |
|                                | TG140       | 140                   | —                                | —        | 0.03      | 0.05      |
| USA                            |             |                       |                                  |          |           |           |
| Mechanical properties          | MD120*      | 120*                  | —                                | 29.3     | 0.03      | 0.025     |
|                                | MD100*      | 100*                  | —                                | 29.1     | 0.03      | 0.05      |
| Leached magnesiothermic        | ML120*      | 120*                  | —                                | 29.1     | 0.02      | 0.025     |
|                                | ML140*      | 140*                  | —                                | 29.1     | 0.03      | 0.05      |
|                                | ML160*      | 160*                  | —                                | 29.1     | 0.03      | 0.05      |
| Leached sodiothermic           | SL120*      | 120*                  | —                                | 29.1     | 0.02      | 0.025     |
|                                | SL140*      | 140*                  | —                                | 29.1     | 0.03      | 0.05      |
|                                | SL160*      | 160*                  | —                                | 29.1     | 0.03      | 0.05      |
| Mechanical properties          | Ti2A*       | <120*                 | 40-70                            | —        | 0.10      | 0.02-0.3  |
|                                | AC2A*       | —                     | >45.5                            | —        | 0.02-0.30 | <0.2      |
| Great Britain                  |             |                       |                                  |          |           |           |
| Leached sodiothermic           | SL120       | 120                   | >45.0                            | —        | —         | —         |
|                                | SL130       | 130                   | 25-35                            | —        | —         | —         |
|                                | SL150       | 150                   | >45                              | —        | —         | —         |
| Japan                          |             |                       |                                  |          |           |           |
| Mechanical properties          | K270        | —                     | 25-35                            | 29.4     | 0.01-0.02 | 0.02-0.03 |
|                                | OT20*       | 20*                   | —                                | —        | 0.01      | —         |
|                                | AI          | 100*                  | —                                | —        | 0.01      | 0.02      |
| West Germany (Krupp, Tikhutan) |             |                       |                                  |          |           |           |
| Mechanical properties          | RT12        | 100-150               | 20-35                            | —        | 0.05      | 0.05      |
|                                | RT16        | 140-200               | 40-55                            | —        | 0.05      | 0.05      |
| France (Pechiney)              |             |                       |                                  |          |           |           |
| Mechanical properties          | T40         | 120-160               | 40.0                             | —        | —         | —         |

Note: Hardness HB measured under 3000-kgf load with the cases marked with the asterisk, where the measure respectively.

- \*1. Book of ASTM Stand., 1958, No. 2, p. 741
- \*2. Kobe Titan brochure, 1961, and Osaka Titanium brochure,
- \*3. Imp. Chem. Ind. (ICI) brochure, Wrought Titanium, 1959.
- \*4. Toho Titanium brochure, 1961
- \*5. Tikhutan brochure, 1962.
- \*6. Pechiney brochure, 1961

by the Magnesiothermic and Sodiothermic Methods

| Composition, %, not above      |      |      |        |       |      |       | Literature source |
|--------------------------------|------|------|--------|-------|------|-------|-------------------|
| Cl                             | Fe   | Si   | N      | Mn    | Mg   | O     |                   |
| USSR                           |      |      |        |       |      |       |                   |
| 0.08                           | 0.07 | 0.04 | —      | —     | —    | 0.04  | MRTU 14-64        |
| 0.08                           | 0.09 | 0.05 | —      | —     | —    | 0.05  |                   |
| 0.08                           | 0.11 | 0.05 | —      | —     | —    | 0.065 |                   |
| 0.10                           | 0.12 | 0.05 | —      | —     | —    | 0.08  |                   |
| 0.10                           | 0.15 | 0.05 | —      | —     | —    | 0.08  |                   |
| USA                            |      |      |        |       |      |       |                   |
| 0.12                           | 0.15 | 0.04 | 0.005  | 0.05  | 0.08 | —     | "                 |
| 0.15                           | 0.45 | 0.10 | 0.005  | 0.20  | 0.10 | —     |                   |
| 0.15                           | 0.10 | 0.04 | 0.02   | 0.04  | 0.4  | —     |                   |
| 0.15                           | 0.25 | 0.10 | 0.05   | 0.20  | 0.5  | —     |                   |
| 0.15                           | 0.25 | 0.10 | 0.05   | 0.20  | 0.5  | —     |                   |
| 0.30                           | 0.12 | 0.04 | 0.0125 | 0.04  | —    | —     |                   |
| 0.30                           | 0.20 | 0.10 | 0.015  | 0.10  | —    | —     |                   |
| 0.30                           | 0.30 | 0.10 | 0.015  | 0.10  | —    | —     |                   |
| —                              | 0.30 | 0.02 | —      | —     | —    | 0.20  |                   |
| —                              | 0.02 | 0.04 | —      | —     | —    | 0.02  |                   |
| —                              | 0.30 | —    | —      | —     | —    | 0.20  |                   |
| Great Britain                  |      |      |        |       |      |       |                   |
| —                              | —    | —    | —      | —     | —    | —     | "                 |
| Japan                          |      |      |        |       |      |       |                   |
| —                              | 0.02 | 0.02 | —      | —     | —    | 0.01  | "                 |
| —                              | 0.20 | 0.10 | —      | —     | —    | 0.20  |                   |
| 0.08                           | 0.08 | 0.02 | 0.002  | 0.005 | 0.24 | 0.02  |                   |
| 0.10                           | 0.05 | 0.01 | 0.003  | 0.01  | 0.23 | —     | "                 |
| West Germany (Krupp, Tirkutan) |      |      |        |       |      |       |                   |
| —                              | 0.20 | —    | 0.0125 | —     | —    | 0.20  | "                 |
| —                              | 0.25 | —    | 0.0125 | —     | —    | 0.25  |                   |
| France (Pechiney)              |      |      |        |       |      |       |                   |
| —                              | —    | —    | —      | —     | —    | —     | "                 |

30-s holding time and 10-mm ball diameter, except for  
 tests were made at 1500 kgf, 30 s, and 10 mm,

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the mechanical properties are regarded as a generalized characterization of the metal's chemical composition. It is obvious that in this case, mechanical properties obtained for the metal by any given method must reflect its chemical composition as accurately as possible and be independent of other factors. Hardness determined on a cast specimen is the mechanical property that meets this condition best [178-181].

#### Influence of Impurities on the Hardness of Sponge Titanium

The following impurities are encountered in appreciable quantities in sponge titanium: nitrogen, oxygen, hydrogen, iron, carbon, silicon, and chlorine. Many investigators have concerned themselves with study of the influence of these impurities on the hardness of ingots melted out of the sponge [178-181, 184]. The influence of the impurities listed above on the properties of technically pure titanium after thermomechanical processing has been the subject of several papers [180, 181].

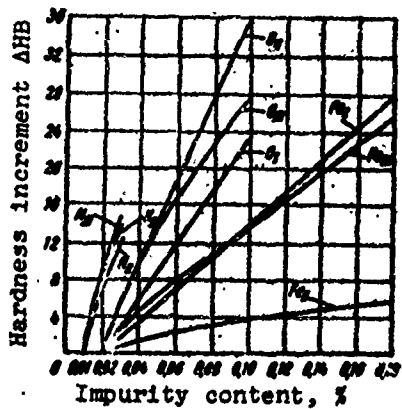


Figure 51. Hardness increase ΔHB of cast specimen as a function of nitrogen, oxygen, and iron contents. I) According to [16]; II) according to [10]; III) according to [11].

Since the hardness of titanium produced by arc remelting is one of the basic criteria that determine sponge quality, a number of authors have studied the influence of impurities on the hardness of control ingots [179-181, 184]. A distinctive feature of Mackinly's method [181] is the addition of various impurities in predetermined amounts to pure titanium sponge. Brown et al. [180] used test results from 152 consignments of sodiothermic titanium produced under industrial conditions and obtained the following relationship between impurity contents and hardness:

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$$HB = 196\sqrt{\%N_2} + 158\sqrt{\%O_2} + 45\sqrt{\%C} + 20\sqrt{\%Fe} + 57.$$

The influence of impurities on control-ingot hardness was studied in [178, 179, 184] by correlation analysis of the results of tests on 2500 industrial consignments of magnesiothermic titanium sponge. It was established that the principal hardening impurities in titanium under industrial conditions are iron, nitrogen, and oxygen.

Figure 51 shows the increases in specimen hardness with changes in the contents of these impurities according to various authors [179-181, 184]. The information given here differs rather substantially as regards the degree to which oxygen influences ingot hardness. This may be because the methods used to determine oxygen content in the sponge were not accurate enough.

The weaker influence of iron on hardness according to Brown is apparently to be explained by the fact that these data were obtained from a study of sodiothermic powder, which differs substantially from magnesiothermic sponge in its iron content and distribution.

The observed fluctuations from 0.01 to 0.04% C and from 0.02 to 0.05% Si in the sponge have little effect on its hardness (at most 8-10 HB units).

#### Sources of Contamination in Titanium Sponge

The average impurity contents in magnesiothermic sponge titanium produced over the long term under industrial conditions are as follows for the blooms: 0.04% O<sub>2</sub>, 0.016% N<sub>2</sub>, 0.06% Fe, 0.030% Si, 0.023% C.

Table 33 lists impurity contents in the titanium tetrachloride, magnesium, and argon typically used under industrial conditions for titanium production [184].

#### Influence of impurities present in the TiCl<sub>4</sub>

About 40% of all the nitrogen, more than 20% of the oxygen, about 15% of the iron, and much of the carbon are introduced into the sponge together with the TiCl<sub>4</sub>. The sponge-hardness increase that results from impurities present in the TiCl<sub>4</sub> represents about

TABLE 33  
Chemical Composition of  $TiCl_4$ , Magnesium, and Argon Used in Titanium Reduction

| Impurity  | Purified $TiCl_4$ , %<br>(by mass) |        |       | Magnesium, %<br>(by mass) |             |       | Argon, %<br>(by mass) |       |         |
|-----------|------------------------------------|--------|-------|---------------------------|-------------|-------|-----------------------|-------|---------|
|           | USSR                               | Japan  | USA   | USSR                      | Japan       | USA   | USSR                  | Japan | USA     |
| Nitrogen  | ~0.0015                            | 0.0015 | —     | ~0.003                    | 0.003       | —     | 0.02—0.2              | —     | 0.00305 |
| Oxygen    | 0.002—0.004                        | Traces | 0.01  | 0.015—0.020               | <0.02       | —     | 0.003—0.045           | —     | 0.00002 |
| Chlorine  | —                                  | —      | —     | <0.007                    | 0.02        | —     | —                     | —     | —       |
| Iron      | 0.004—0.006                        | 0.002  | 0.001 | 0.02—0.035                | 0.02—0.03   | 0.03  | —                     | —     | —       |
| Silicon   | 0.006                              | 0.0014 | 0.001 | <0.01                     | 0.002—0.004 | 0.006 | —                     | —     | —       |
| Vanadium  | 0.004                              | 0.0001 | 0.001 | —                         | —           | —     | —                     | —     | —       |
| Sulfur    | Not det.                           | None   | —     | —                         | —           | —     | —                     | —     | —       |
| Aluminum  | 0.004                              | —      | —     | <0.006                    | 0.002       | 0.003 | —                     | —     | —       |
| Copper    | —                                  | —      | —     | <0.002                    | 0.001       | 0.003 | —                     | —     | —       |
| Zinc      | —                                  | —      | —     | —                         | 0.003       | —     | —                     | —     | —       |
| Manganese | —                                  | —      | —     | —                         | 0.003       | 0.00  | —                     | —     | —       |
| Nickel    | —                                  | —      | —     | <0.002                    | —           | 0.001 | —                     | —     | —       |

40% of the total increment from introduction of impurities by all other sources.

The elementary composition of the  $TiCl_4$  has not yet been studied thoroughly enough, although about 20 impurities of inorganic and organic origin have already been identified in it and it was assumed until recently that there were only six ( $SiCl_4$ ,  $AlCl_3$ ,  $VOCl_3$ ,  $FeCl_3$ ,  $COCl_2$ , and chlorine). More than 4 tons of  $TiCl_4$  are used for each ton of titanium sponge. Practically all of the impurities are transferred from the  $TiCl_4$  into the sponge, so that the impurity contents in the metal will be more than 4 times the levels in the  $TiCl_4$ .

A certain amount of dissolved air may also be present in the  $TiCl_4$  in addition to the bound oxygen and nitrogen [184, 185]. This requires filling the systems used to store the purified  $TiCl_4$  and transport it to the reduction reactors with an inert gas that prevents the  $TiCl_4$  from reacting with air.

Influence of impurities present in the magnesium

About 20% of the  $N_2$ , 40% of the  $O_2$ , and 15% of the Fe are introduced into the sponge together with the magnesium. The sponge-hardness increment due to the impurities present in the

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magnesium is about 30% of the total hardness rise.

Under typical industrial conditions, the magnesium is loaded into the reactor at the beginning of the reduction process in an amount sufficient to support the entire cycle without replenishment. The mass of the magnesium in the reactor is then 1.5 times the mass of the commercial titanium sponge produced. Since most of the impurities will be transferred from the magnesium into the titanium sponge, their contents in the sponge will be 1.5 times higher than in the magnesium.

However, it must be remembered that when  $TiCl_4$  is fed into a reactor holding liquid magnesium under these conditions, the impurities present in the magnesium will interact primarily with the  $TiCl_4$  and with the titanium that has formed, and will be deposited on the floor and walls of the reactor. Adsorption of these impurities on the surface of the titanium sponge formed early in the process is another possibility. Hence the sponge that is deposited on the bottom and walls of the reactor during the first phase of the process is more heavily contaminated by impurities than the basic mass of the sponge; during processing of the block, these parts of the sponge must be removed and scrapped. Thus, the magnesium is purified of most of its impurities in the reactor at the start of the process. There are known methods for purifying the magnesium before placing it in the reactor by pretreatment with titanium tetrachloride in a special apparatus. (1)

To improve the quality of magnesium for use in reduction of  $TiCl_4$ , it is necessary to prevent its contamination by improving the purity of the raw material used in the magnesium electrolyzers to produce the magnesium, to electrolyze the magnesium at the lowest possible temperatures, to store it in mixers, and to transport the purified molten magnesium and load it into the reduction reactors under conditions that prevent it from interacting with air. Transfer of the magnesium through pipes with electromagnetic or induction pumps and filtration of the metal through cermet filters, and titanium filters in particular, are promising [184].

Footnote (1) is on page 325.

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| Argon, %<br>(by mass)                  |       |         |
|--|-------|---------|
| SSR                                    | Japan | USA     |
| 0.2                                    |       | 0.00005 |
| 0.045                                  |       | 0.00002 |
| O <sub>2</sub> + N <sub>2</sub> < 0.01 |       |         |

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Recent research indicates that if special measures are observed, unrefined magnesium taken directly from magnesium electrolyzers can be used in reduction reactors [330].

#### Contamination of titanium by reactor material

About 50-70% of the iron present in titanium sponge enters it as a result of reactions between the titanium and the reactor material. The melting point of the eutectic Ti-Fe alloy is about 1085°C. Use of type 1Kh18N9T chrome-nickel steel results in the formation of a complex eutectic alloy with a melting point of 980-1000°C. Since the reduction process is carried out at temperatures up to 900°C and the separation at temperatures up to 1050°C, the titanium may alloy very rapidly with the reactor material. The rate and depth of mutual diffusion between titanium and iron are quite high. Moreover, the titanium sponge is contaminated by nickel and chromium as well as iron when chrome-nickel steels are used as reactor materials.

The iron, nickel, and chromium used in the reactor material interact with the titanium; they also dissolve in fused magnesium. The reactor material interacts with  $TiCl_4$  at high temperatures. It has been established that titanium tetrachloride reacts slowly with the reactor material up to 600°C, but that the rate of the interaction rises sharply at higher temperatures. About 20-25% of the total iron enters the sponge as a result of solution of reactor material in the magnesium and the interaction with  $TiCl_4$ . It has recently been found that among the suitable structural materials, types OKh17, 1Kh13, Kh25T, and other chrome steels are more stable in the presence of magnesium and titanium tetrachloride than St. 3 and 1Kh18N9T [184].

It has been established that a major part of the impurities from the reactor material into the titanium during vacuum separation, especially in the last phase, when the temperature at the wall-titanium interface is highest. In work with reactors made from St. 3 steel, it is necessary to watch carefully for the formation of scale on the inner surface of the reactor as it is being prepared for the process. It is also necessary to remember

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the possibility of surface melting of the heat shields installed in the reactor, which may also contaminate the titanium sponge.

To protect the titanium sponge from contamination by impurities transferred into it from the reactor material, it is necessary to lower the temperature and shorten the cycle time in reduction and vacuum separation, to remove heat shields from the reaction zone, and to use reactors made from steels that react minimally with titanium sponge, magnesium, and titanium tetrachloride.

Great interest attaches to reactors with two layers of steel -- an outer layer that resists scaling and an inner layer made from a steel with less tendency to react with titanium, magnesium, and  $TiCl_4$ . Use of titanium for the inner reactor layer is effective. Then, however, the sponge welds very tight to the titanium walls, as we indicated above, and this greatly complicates extraction of the sponge from the reactor. Various coatings, including nickel-plating,<sup>(2)</sup> have been proposed for the reactor inner walls to prevent interaction between the titanium and the reactor material.

#### Influence of chlorine

As a rule, chlorine is present in magnesiothermic titanium sponge in amounts from 0.02 to 0.12% Cl. During remelting of the titanium sponge, all of the chlorine is eliminated from the metal, and it has no marked effect on ingot quality.

A misconception that prevailed at one time was that all of the chlorine present in the titanium sponge was bound to magnesium as the chloride, which did not distill out of the sponge during vacuum separation. It was considered impossible for other chlorides, such as those of calcium, manganese, chromium, lower titanium chlorides, and others, as well as chlorine and hydrogen chloride absorbed on the sponge surface to exist in the sponge. However, the fact that the chlorine content in the sponge is always somewhat larger than the amount that the magnesium present in the sponge could bind demonstrates that not all of the chlorine present in the sponge is bound into magnesium chloride. Moreover,

Footnote (2) is on page 325.

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industrial practice has shown that even substantial increases in temperature, hardness of vacuum, and vacuum-separation time do not remove all of the chlorine from titanium sponge, indicating the presence of less volatile chlorine compounds in the sponge. This may, of course, be due to some degree to the fact that part of the magnesium chloride is in closed pores deep inside the sponge, from which removal of the vapors is difficult.

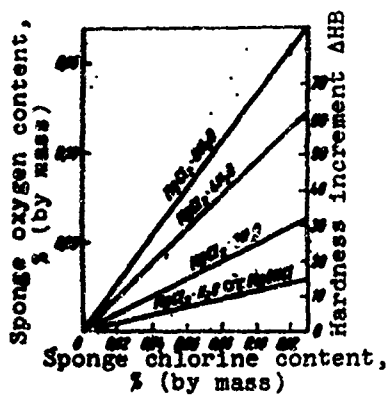


Figure 52. Oxygen content in sponge and hardness increase of cast specimen as functions of its content of chlorine bound in magnesium crystal hydrates.

sponge, some of the oxygen present in the water of crystallization enters the metal, to the detriment of its properties.

Figure 52 shows sponge oxygen content and the increment in the hardness of the metal as functions of sponge chlorine content and the amount of water in crystal-hydrate form. The hardness increment was computed as a function of oxygen content after MacKinly [181].

When the crystal hydrates are heated to 182°C, removal of water lowers the content to 2 moles per mole of  $MgCl_2$ . Further heating hydrolyzes the dihydrate and forms the compound  $MgO$ .

As we know, magnesium chloride is an extremely hygroscopic compound, forming crystal hydrates with 1 to 12 water molecules on interaction with moist air. Hydrates containing 6, 4, and 2 molecules of water exist at temperatures above 0°C. Since the titanium sponge, which contains magnesium chloride, is exposed to air during extraction from the reactor, crushing, and preparation for melting, the magnesium chloride may take up as many as 6 moles of water per mole of  $MgCl_2$ . During remelting of such

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All of the oxygen present in the MgO is transferred into the titanium when the sponge is remelted in vacuum arc furnaces. Thus, in analyzing the effects of chlorine on sponge oxygen content and hardness, it is necessary to use a relationship that connects these quantities when an oxygen source is present in the sponge in the form of MgO. As we see from Fig. 52, a 0.01% increase in chlorine content results in an increase of about 0.004% in oxygen content and an increase in hardness by 2 HB units.

These increases in oxygen content and hardness occur if all of the magnesium chloride present in the sponge has been hydrolyzed. However, as we indicated above, some of the magnesium chloride is in closed pores and therefore cannot interact with atmospheric moisture. This is supported by the studies of V.V. Sergeev et al. [189], who established that the relative oxygen-content and hardness increments are smaller when the chlorides are thoroughly distilled out of the sponge (down to 0.06-0.08% Cl) than at chlorine contents above 0.08-0.10%. The authors of [189] take this as an indication that much of the chlorine is in closed pores in the sponge at chlorine contents below 0.06-0.08%. Since it is not possible under ordinary vacuum-separation conditions to remove chlorine from the sponge down to contents of less than 0.02-0.05%, it must be assumed that this amount of chlorine is either in closed pores or bound in less volatile chlorides. All of this indicates that the influence of chlorine on sponge oxygen contamination and hardening should be somewhat weaker than Fig. 53, a and b, indicates. It has been established in practice that 0.01% of Cl increases the hardness of the metal by 1-1.5 HB units, which corresponds to an increase in sponge oxygen content by ~0.002%.

To prevent contamination of the titanium with oxygen from MgO, it is necessary to carry the vacuum-separation process to the point of maximum removal of magnesium chloride from the sponge. Here, however, it must be remembered that extending the vacuum-separation process cannot lower the chlorine content much below the limits indicated, and that seepage of air into the vacuum unit may inject the titanium sponge with more oxygen than

Graphic Not Reproducible



Figure 53. Structure of titanium sponge obtained from various points in reactor. The numerals indicate the density of the sponge.

separation, and to provide for storage of the sponge in airtight containers. As we indicated earlier, containers filled with sponge are sometimes evacuated and then filled with a dry inert gas. In some cases, a special container with a compound that is more hygroscopic than  $MgCl_2$ , such as  $AlCl_3$ , etc., is placed in the container with the sponge<sup>(3)</sup>[199].

Good results are obtained by drying the sponge before melting, or consumable electrodes pressed from it, at 80-100°C. It

Footnote (3) is on page 325.

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the residues of magnesium chloride that have not been driven out of the sponge can bind. In addition, as the separation time is extended, the sponge also becomes contaminated by iron and nitrogen owing to the reaction with the reactor material.

It is therefore very important to establish an optimum permissible chlorine content in the sponge and optimum temperatures and times for the vacuum-separation process. In most cases, the permissible amount of chlorine in magnesiothermic titanium sponge is 0.08-0.15% (see Table 32). G.M. Vaynshteyn et al. [106, page 88] found that variation of sponge chlorine content in the 0.08-0.12% range has no marked influence on the mechanical properties of ingots and sections cast from this sponge and does not complicate sponge-melting technology.

To prevent deterioration of sponge quality as a result of hydrolysis of  $MgCl_2$ , it is also necessary to minimize the time of contact between moist air and the reaction mass after reduction and the titanium sponge after vacuum

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has been established under laboratory conditions that drying the sponge before remelting removes practically all moisture residues from it and thus prevents hardness increase in the ingots cast from it. It has been demonstrated that all moisture can be removed from the sponge by vacuum-treating it at temperatures above 40°C; moisture can be eliminated completely from a pressed consumable electrode in a vacuum at 100°C [190, 207].

#### Influence of other contamination sources

Seepage of air into the reduction reactor and especially into the separation reactor is an important source of titanium-sponge contamination by oxygen and nitrogen.

Normally, air leaks into a cold separator at 1.0-2.0  $\mu\text{m}/\text{min}$ . The hardness increase that results from the higher oxygen and nitrogen contents in the sponge may range from 5.0 to 10 HB. Obviously, somewhat more air will seep into a hot unit than into a cold one.

The inert gas forming the atmosphere for the reduction and vacuum-separation processes is another source of oxygen and nitrogen contamination of the sponge. To purify the inert gas before feeding it into the reactor, it is passed through a layer of titanium sponge that has been heated to 800-900°C and placed in a special retort mounted in the electric furnace [184].

Titanium sponge may be contaminated by oxygen and nitrogen during its removal from the reactor and during crushing. This makes it desirable to remove the sponge from the reactor with a minimum of mechanical effort and not to permit overgrinding of the titanium sponge during crushing and milling.

Titanium sponge may be contaminated by carbon, which enters it together with oil vapor during vacuum separation. This occurs in the event of vacuum-pump shutdown without actuation of the system's vacuum shutoff. The incandescent titanium sponge then acts as a getter, the pressure in the reactor drops, and vacuum-oil vapor is sucked into it from the vacuum system.

Distribution of Impurities in the Sponge and Homogeneity of Commercial Consignments

Uniformity of chemical composition and mechanical properties is one of the basic indicators that determine the quality of sponge titanium, since it determines to a substantial degree the uniformity of titanium ingots cast from the sponge and titanium rolled products. The rather high reduction rate of titanium ingots and rolled stock that now prevails is a consequence of their chemical-composition and mechanical-property nonuniformity.

Consignments of commercial titanium sponge weighing up to 4-8 tons are currently made up from metal obtained in several reactors. From 500 to 1500 kg of titanium sponge are extracted from each reactor after the process. It is therefore necessary to blend the sponges produced in several reactors in order to produce a commercial lot. Under these conditions, it is very important that the sponge in each reactor taken separately and that from all reactors whose metal is taken to make up a commercial consignment be uniform.

However, owing to peculiarities of the magnesium reduction of  $TiCl_4$  and vacuum separation of the reaction mass, the impurities present in the titanium block are not uniformly distributed.

However, statistical reduction of the results obtained from determination of chemical composition for samples taken at various points in a block of titanium sponge indicate that the impurities are distributed in characteristic zones of the block if the composition of the starting materials is kept constant and the reduction and separation processes are carried out under standard conditions. This makes it possible to remove a substantial part of these impurities from the titanium sponge during cutting and grinding of the block [172].

The liner section of the sponge, which has a developed surface, is first to interact with air that seeps into the reactor and with the nitrogen and oxygen present in the argon with which the reactor is supplied. Lower titanium chlorides and dispersed magnesium are often found on the surface of the lining sponge

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during the reduction process. When the reactor is opened, the lower titanium chlorides and disperse magnesium oxidize and contaminate the sponge (especially the lining) with oxygen.

The magnesium chloride becomes saturated with water when the reduction reactor holding the reaction mass is disassembled and the mass is brought into contact with air. The lining sponge and the surface layers of the main titanium-sponge block are first to be saturated with moisture. In the subsequent vacuum-separation process, oxygen enters the sponge from the hydrolyzed magnesium chloride.

The surface layers of the sponge, which come into contact with the reactor material, contain substantial amounts of iron and carbon, as well as nickel, chromium, and manganese if the reactor is made from stainless steel.

The bloom section of the titanium sponge is purest and most uniform, provided that  $TiCl_4$  and argon of the same composition have been fed into the reactor throughout the reduction process.

During processing of the titanium block, its bottom and liner, the surface layers of the sponge, and the film are separated from it to obtain high-grade uniform metal and used after special purification to make up lower-grade commercial consignments. After removal of the contaminated metal, the main bloom of the block is processed and consigned separately.

Owing to peculiarities of the reduction and vacuum-separation processes, the titanium sponge varies in structure and density. Figure 53 shows typical sponge structures and densities in various reactor zones. Granulometric compositions and specific surface areas of titanium sponge are listed in Tables 35 and 36 (see pages

Uniformity of the metal in commercial consignments is ensured by blending matched sponges with the closest similarity of chemical composition and mechanical properties. Usually, it is sufficient to know the chlorine content and hardness of the sponge obtained from each reactor to make up a uniform blend.

After batching and thorough blending, chemical composition and hardness are determined for a cast specimen smelted out of a general sample taken from the over-all charge, so that commercial consignments of metal with uniform composition and mechanical properties are obtained [12, 16].

Inclusions of gas-saturated and iron-alloyed metal that are encountered in titanium sponge cause considerable difficulty in rolling titanium ingots. In some cases, these inclusions may not be thoroughly melted during remelting of such sponge in vacuum-arc furnaces, and they may enter the ingot in the form of inhomogeneous inclusions. When these ingots are rolled, the defects cause exfoliation of semifinished products and form large inclusions in them, so that their mechanical properties drop sharply and they must be rejected.

To prevent such inclusions from entering the ingots, it is necessary to prevent softening of the reactor, to remove oxidized areas completely from the surface of the titanium block, and to cut off the surface layer and films before breaking up the sponge. During milling, it is extremely important to avoid overrefinement of the sponge, since this results in vigorous oxidation. Moreover, it is extremely difficult to remove inclusions from a finely crushed product. The sponge must be carefully graded after crushing, during which the opportunities for oxidation must be minimized.

To prevent small inclusions from entering critically stressed products, the use of fine sponge should be avoided in smelting out ingots and making semifinished pieces that will go into products of which high reliability, stability, and strength are required in heavy-duty operation. Use of fine sponge should be limited for the most part to smelting ingots for less vital applications.

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#### Footnotes

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| 315 | <sup>1</sup> Patent (Japanese), No. 8953, 1957.   |
| 317 | <sup>2</sup> Patent (Japanese), No. 10,457, 1957. |
| 320 | <sup>3</sup> Patent (USA), No. 2,841,487, 1956.   |

## Chapter 15

### REDUCTION OF TITANIUM TETRACHLORIDE BY SODIUM

#### History of Development of the Sodiothermic Method

Like magnesium, sodium is one of the most common elements in nature. Its content in the earth's crust is 2.4%. In the table of abundances in the earth's crust, sodium comes after oxygen, silicon, aluminum, iron and calcium. Vast deposits of rock salt and a highly developed industry that produces the metal by electrolysis of sodium hydroxide or fused sodium chloride, together with the comparatively moderate cost of metallic sodium, make this metal available for use as a reducing agent in the production of titanium.

In 1966, world sodium production (outside of the USSR) came to about 250-300 thousand tons per year, of which about 50% were produced by electrolysis of fused sodium chloride in Downs electrolyzers. Sodium produced by this method is distinguished by rather high purity (99.6%).

Sodium has a high affinity for chlorine ( $-\Delta Z_{\text{NaCl}}^{\circ} = 56.5$  kcal/g-atom of chlorine), which is 13.5 kcal/g-atom of chlorine higher at 800°C than the affinity of titanium to chlorine ( $-\Delta Z_{\text{TiCl}_4}^{\circ} = 13.5$  kcal/g-atom of chlorine); this is sufficient for complete reduction of  $\text{TiCl}_4$  by metallic sodium. Titanium and sodium are practically insoluble in one another.

All of these factors taken together with the technological aspects of the reduction process make sodium one of the most promising reducing agents for the organization of a modern large-scale, high-efficiency titanium-producing process.

Titanium tetrachloride was first reduced to the metal and to  $TiCl_3$  [sic] with sodium in 1875 by the Russian scientist D.K. Kirillov [209]. Attempts made earlier by Berzelius (1825), Wohler (1857), and a number of other scientists to reduce potassium fluotitanate with sodium had not produced the desired result -- no metallic titanium was formed. Only in 1887, i.e., 12 years after D.K. Kirillov, did Nilson and Petersson succeed in preparing metallic titanium by reducing  $TiCl_4$  with sodium in a steel bomb [274]. Using a similar method, Moissan obtained 95% pure titanium in 1890 [66, 275]. Pure titanium (about 99.9%) was produced by Hunter et al. in 1910 by sodium reduction of specially purified titanium tetrachloride in an evacuated steel bomb [67]. These experiments were reproduced by Lely and Hamburger [278] in 1914, and the process was later studied by Belle [279] in a somewhat modified form (using sodium hydride as the reducer).

We see from the above that the sodiothermic method of reducing titanium was developed under laboratory conditions at a somewhat earlier date than the magnesiothermic method. However, major difficulties that arose in work with such a chemically active metal as sodium, the need to carry out the process in a bomb, and the long-standing idea that the process represented an explosion hazard slowed the development of the sodiothermic method. On the basis of these difficulties, Kroll, the originator of the magnesiothermic method, regarded the sodium reduction of titanium tetrachloride as altogether hopeless [245].

However, experiments carried out with the method in 1940-1943 by the German firm Degussa indicated that the process could be carried out in an inert atmosphere at standard pressure [280]. This method was applied on a rather large scale in Germany to produce titanium powder for use in igniter charges and as a getter in vacuum electronics. The reduction was carried out in an iron pot

In a sealed reactor. The reaction mixture, which consisted of a eutectic mixture of sodium and potassium chlorides in 1:1 proportions and metallic sodium, was fused, gaseous titanium tetrachloride was fed into the melt, and an agitator was started to stir the bath. The end of the process was indicated by jamming of the agitator by the titanium that had accumulated in the reactor.

The sodiothermic process was later improved in England, which had a developed metallic-sodium industry; the production of magnesium in England was and remains quite limited owing to the absence of a cheap magnesium raw material. In 1951, the British firm Imperial Chemical Industries (ICI), one of the main producers of metallic sodium, began to operate an industrial sodiothermic installation with a capacity of 150 tons of titanium per year, whose reactors had a cycle output of about 45 kg of titanium [281, 282]. In 1955, the same firm built a sodiothermic plant with a capacity of 1500 tons of titanium per year at Wilton, Yorkshire; it used a sealed steel reactor in which the reduction was carried out in an inert-gas atmosphere at an excess pressure of about 220-300 mm Hg.

Successful assimilation of the sodiothermic method by the British firm ICI contributed to its introduction in the American titanium industry. In 1956, under license from ICI, the American firm Electrometallurgical placed a 6750-ton/year sodiothermic plant in operation at Ashtabula, Ohio. By this time, the technology and equipment of the sodiothermic process had been improved to the extent that this plant was working at capacity within 8 months [97, 286].

In 1958, the firm Industrial Chemicals placed the USA's second sodiothermic plant, one with a capacity of 4500 tons of titanium per year, in operation at Ashtabula. According to available information, this plant uses improved semicontinuous reduction equipment [245]. Plans were made to build at least two more sodiothermic plants in the USA, at Natrium, West Virginia and Wilmington, North Carolina, with a total capacity of 11,800 tons [94]. However, neither of these plants was built because of

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the sharp drop in titanium production in the USA that began in 1957 for the reasons discussed above.

In the Soviet Union, the sodiothermic method of reducing titanium has been successfully developed and mastered under laboratory and pilot-plant conditions in complex with the preparation and purification of the sodium and hydrometallurgical refinement of the reaction mass.

The sodiothermic method has the following important advantages over the magnesiothermic reduction of titanium:

1. Because of the higher chemical activity of sodium, the rate of the sodiothermic reduction of titanium is considerably higher than that of the magnesiothermic method. This permits a sharp increase in reactor productivity and reduces unit capital investment for the construction of sodiothermic plants.

2. The coefficient of sodium utilization in the reduction reactor is almost 100%, while the corresponding figure for magnesium does not exceed 60-70%. The cost of the reducing agent is lower in the sodiothermic than in the magnesiothermic method (in the USA, by about 30-35%).

3. The reaction mass obtained as a result of sodiothermic reduction can be processed by hydrometallurgical methods (leaching out in a dilute hydrochloric acid solution). This permits the use of inexpensive, highly productive apparatus, a respect in which this method compares favorably with the expensive and relatively unproductive vacuum-separation process used to purify the reaction mass in the magnesiothermic process.

4. The titanium is obtained in the form of a fine powder in the sodiothermic reduction. This makes it much easier to prepare a homogeneous charge and pour more uniform titanium ingots.

5. Use of sodium as the reducing agent opens prospects for the development and implementation of semicontinuous and eventually continuous processes for the reduction of titanium.

6. Reducing the titanium tetrachloride through the lower chlorides in two stages produces titanium of higher purity. This

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modification of the sodiothermic process permits regeneration of the low-grade titanium and titanium scrap into a high-quality product.

However, the sodiothermic method also has disadvantages that must be borne in mind in comparing it with the magnesiothermic process.

1. The need to take special precautionary measures and ensure high reliability and good sealing of the equipment, since the sodium used has high chemical activity. When these conditions are observed, however, work with sodium becomes quite safe.

2. Conduct of the reduction under conditions such that, because of peculiarities of the technological process, the sodium chloride that accumulates in the reactor is not withdrawn from it during the reduction process, as in the magnesium reduction of  $TiCl_4$ . As a result, the capacity of the sodiothermic reactor is utilized less efficiently than that of the magnesiothermic reactor.

3. The heat effect of the reactions in which  $TiCl_4$  is reduced by sodium under standard conditions is 66% larger than when magnesium is used as the reducing agent. For this reason, heat must be taken out of the reactor more rapidly during the sodiothermic reduction, and the system that measures and regulates process parameters must be more sophisticated. The need for precision temperature control in the reactor is also dictated by the narrow interval between the melting point of sodium chloride ( $801^\circ C$ ) and the boiling point of sodium ( $883^\circ C$ ).

#### Physicochemical Background of the Process and the Mechanism of the Reduction Reactions

The over-all reaction in which titanium tetrachloride is reduced by sodium can be represented as stepwise reduction of titanium chlorides by the scheme

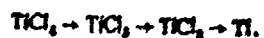


Figure 54 presents curves of the free-energy changes for the reactions in which titanium tetrachloride can be reduced by sodium, and for certain secondary reactions, as calculated by the Temkin-

Schwartzmann method described above on the basis of the starting data in Table 29 (see pages 228 and 229). The calculations were made for the case in which liquid titanium tetrachloride and fused sodium are injected into the reactor, i.e., under conditions similar to those under which industrial reactors are operated.

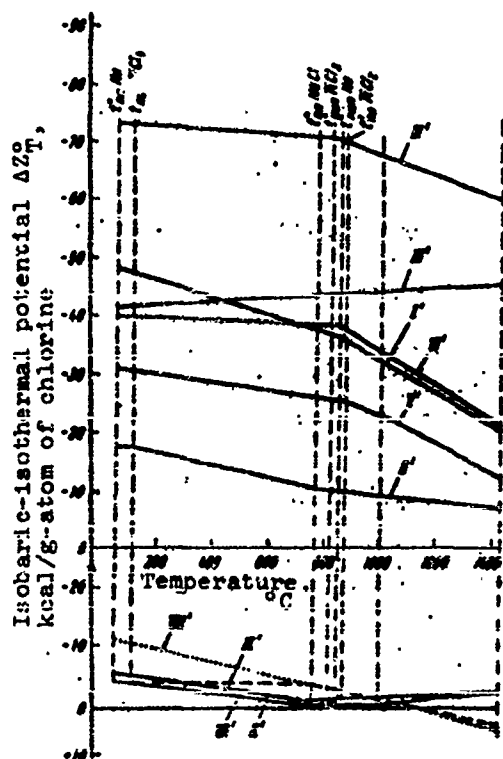
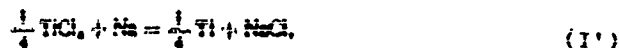
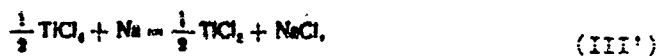


Figure 54. Temperature curves of isobaric-isothermal potentials for the sodiothermic reduction reactions of titanium chlorides.

As we see from Fig. 54, the following reactions are thermodynamically possible in the sodium reduction of titanium tetrachloride:





Also possible in the system are secondary reactions in which metallic titanium interacts with  $\text{TiCl}_4$  and the lower titanium chlorides and reactions among the lower titanium chlorides:



As we know, the direction taken by a chemical reaction depends to a substantial degree on the physical states and equilibrium partial pressures of the reactants and the reaction products. These data are given in Table 30.

The nature of the reduction process is decisively influenced by the reactions of the sodium and the titanium chlorides formed in the reduction with the sodium chloride, which is in this case the environment in which many of the reactions examined above take place.

The fusibility diagram of the Na-NaCl system was investigated by Bredig et al. [258]. It was found that the system has a eutectic at 1.5-2.0% (atomic) of Na, with a melting point of about 790°C. Above 1050°C, all of the sodium dissolves in NaCl. In the range of working process temperatures in the sodiothermic reduction of titanium (850-920°C), the solubility of sodium in NaCl ranges from 7 to 17%.

Ehrlich et al. [259] studied the phase diagram of the  $\text{TiCl}_3$ -NaCl system (Fig. 55). This diagram shows that at 25% (molecular) of  $\text{TiCl}_3$ , the liquidus line has a peritectic point at 553°C. The system also has a eutectic at a 40% content (molecular) of  $\text{TiCl}_3$ , with a melting point of 462°C. Beyond the eutectic point, the liquidus line proceeds without inflections to the melting point

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of  $TiCl_3$ . Thus, only the single chemical compound  $3NaCl \cdot TiCl_3$  has been identified in the  $NaCl-TiCl_3$  system. It has also been concluded on the basis of the trend of the liquidus line and data on the heats of formation and activities of the salts that complex  $[TiCl_6]^{+3}$  ions exist in this system up to a content of 12% (molecular) of  $TiCl_3$  in the melt, and that appreciable dissociation of the complex ions begins at higher  $TiCl_3$  concentrations.

The  $NaCl-TiCl_3$  system was also studied up to a content of 22.4% (mol.) of  $TiCl_3$  by M.V. Kamenetskiy [262], who established the presence of a eutectic at 22.4% (mol.) of  $TiCl_3$  with a melting point of  $540^\circ C$ ; other investigators have been G.V. Chernov,<sup>(1)</sup> Clark [263], and Mellgren [264].

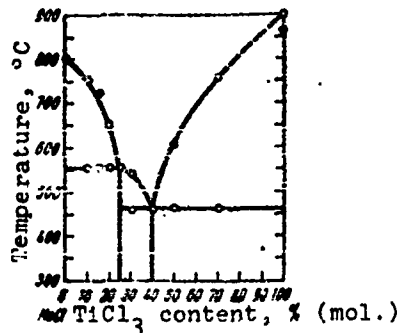


Figure 55. Phase diagram of  $NaCl-TiCl_3$  system.

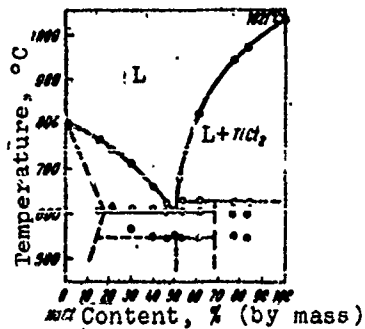


Figure 56. Phase diagram of  $NaCl-TiCl_2$  system.

In the  $NaCl-TiCl_3-TiCl_2$  system, S.V. Ogurtsov, V.A. Reznichenko, and S.I. Yegorov [106, page 60] identified a compound corresponding to the formula  $13NaCl \cdot 3TiCl_3 \cdot 2TiCl_2$ , containing about 50% of the lower titanium chlorides and melting at about  $502^\circ C$ . This compound, which they named "black salt," undergoes practically no disproportionation and is therefore highly suitable for reduction.

The  $NaCl-TiCl_2$  system was investigated in detail by Komarek and Kerasimenko [265, 266]. Figure 56 shows the phase diagram that they established for it. We see from this diagram that the system has one eutectic at 50% (by mass)  $TiCl_2$ , with a melting

Footnote (1) is on page 359.

point of 605°C, and two peritectic compounds. One of the NaCl·TiCl<sub>2</sub> forms at a content of about 50% TiCl<sub>2</sub> and melts at 628°C, while the other, 2NaCl·TiCl<sub>2</sub>, decomposes in the solid state at 546°C. The presence of these compounds in the NaCl·TiCl<sub>2</sub> system is confirmed by x-ray structural analysis.

The temperature curve of free energy established by Komarek and Herasimenko on the basis of the phase diagram of the NaCl-TiCl<sub>2</sub> system suggests that liquid NaCl·TiCl<sub>2</sub> melts are most stable at temperatures around 800°C and the component proportions Na:Ti:Cl = 2:1:4.

Thus, the existence of [TiCl<sub>4</sub>]<sup>-2</sup> complex ions in this system is highly probable.

The phase diagrams of the sodium (potassium) chloride-titanium dichloride systems have also been studied by Mellgren [264], Krey and Kellogg [267], Ehrlich and Kuhne [268], Yu.V. Baymakov [269], A.M. Budnevskiy [270], and other authors [271; 178, page 205; 135, page 73].

It was established by B.V. Markov that equilibrium intervenes in the NaCl-TiCl<sub>2</sub>-TiCl<sub>3</sub>-TiCl<sub>4</sub> system at contents of 35-40% TiCl<sub>2</sub> and 65-60% TiCl<sub>3</sub> [271]. Boozenny [272] investigated equilibrium in the Na-TiCl<sub>2</sub>-TiCl<sub>3</sub>-NaCl system. Calculations based on his experimental data yielded the following results. For NaCl melts containing small amounts of dissolved TiCl<sub>2</sub> and Na at 850°C, the equilibrium TiCl<sub>2</sub> and Na concentrations are determined by the equation

$$\frac{C_{Na}^0}{C_{TiCl_2}^0} = 1.6 \cdot 10^{-18}. \quad (11)$$

For NaCl melts containing dissolved TiCl<sub>3</sub> and TiCl<sub>2</sub>, the equilibrium TiCl<sub>2</sub> and TiCl<sub>3</sub> concentrations at 850°C are determined by the equation

$$\frac{C_{TiCl_2}^0}{C_{TiCl_3}^0} = 2.0 \cdot 10^{-2}. \quad (12)$$

In a study of the activity coefficients of TiCl<sub>3</sub> and TiCl<sub>2</sub> in NaCl, Boozenny established that TiCl<sub>3</sub> is associated with NaCl to a substantially greater degree than is TiCl<sub>2</sub>.

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There are practically no data available on the state of the NaCl-TiCl<sub>4</sub> system, and the conclusions drawn by the individual investigators are contradictory. Thus, M.V. Kamenetskiy reports [262] that this system is extremely stable, but more recent studies by Ehrlich [259] indicate its instability. Obviously, Ehrlich's data are more reliable. Kroll's data [260] suggest total insolubility of TiCl<sub>4</sub> in NaCl. It was found in experiments conducted by Smolinsky, Hannam and Leach that about 1% TiCl<sub>4</sub> dissolves in NaCl [270].

As we see from the temperature curve of free energy for the reaction of titanium tetrachloride with sodium (see Fig. 54), the reduction reactions may proceed at relatively low temperatures from the thermodynamic standpoint. However, they advance at appreciable rates beginning at temperatures above 200°C.

For study of the directions taken by the reduction reactions and their mechanisms, and to investigate the feasibility of sodio-thermic reduction of titanium with periodic sodium supply to the reactor, it is helpful to consider 2 temperature ranges:

from 200 to 700°C, i.e., from the temperature at which the reaction rate becomes appreciable to the temperature at which easily fusible sodium chloride and titanium chloride salt melts form in the system;

from 700 to 980°C, i.e., from the temperature at which these salt melts form in the system to the maximum possible temperature of the reduction process (or, in other words, to the temperature at which the eutectic alloy forms at the interface between the reduced metallic titanium and the reactor material).

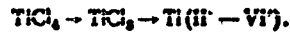
Temperature range from 200 to 700°C

As we see from Fig. 54, the direct reduction of TiCl<sub>4</sub> to metallic titanium (I') is thermodynamically most probable in the range from 200 to 450°C, and the reduction of TiCl<sub>4</sub> to TiCl<sub>2</sub> (III') between 450 and 700°C.

However, because metallic titanium is insoluble in molten sodium, reaction (I') becomes difficult, since the minute particles of reduced titanium coat the surface of the sodium chloride

and, to some extent, the sodium, forming a dense conglomerate. This creates conditions favoring the secondary reactions of titanium with the tetrachloride (VII') and (VIII'), although the thermodynamic probability of these reactions is low, especially with an excess of sodium.

The reaction in which  $TiCl_4$  is reduced to  $TiCl_2$  (III') is thermodynamically possible in this temperature range. However, in view of the considerably higher vapor pressure of  $TiCl_3$  as compared with that of  $TiCl_2$  at 200-700°C, preference should be given to the reduction of  $TiCl_4$  to  $TiCl_3$  (II'). Moreover, the equilibrium concentration of  $TiCl_3$  in the  $TiCl_3$ -NaCl system is considerably higher than that of  $TiCl_2$  in the  $TiCl_2$ -NaCl system [99]. These factors, together with the sluggish reduction of  $TiCl_2$  to Ti (V') [52], suggests that occurrence of the reactions in accordance with the scheme already cited is most probable under these conditions:



In the gaseous phase, in consideration of the high vapor pressures of  $TiCl_4$ , Na, and  $TiCl_3$ , preference must be given to the direct reduction of  $TiCl_4$  to titanium (I') and the reduction of  $TiCl_4$  to  $TiCl_3$  (II'). From the kinetic standpoint, reaction (II') is more probable than (I'), since the molar proportions of the compound to be reduced and the reducing agent are 1:1 in reaction (II') and 1:4 in (I'). From the same point of view, the rate of the direct reduction of  $TiCl_4$  to Ti in the gaseous phase is higher than the rate of the stepwise reduction via  $TiCl_3$  and  $TiCl_2$  to titanium.

These conceptions of the course taken by the reactions in the 200-700°C temperature range are in good agreement with the results of laboratory studies and with practical reduction of  $TiCl_4$  with sodium under industrial conditions.

Thus, S.V. Ogurtsov et al. [106, page 11] established in laboratory studies that even at the very beginning of the process, the surface of the metallic sodium is coated by a dense crust consisting of a mixture of fine titanium (up to 20%) and sodium chloride particles. This crust is detrimental to contact between

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the sodium and the  $TiCl_4$ , so that Reaction (I') subsides and the secondary reactions (VII')-(X') develop. Agitation of the reaction mass during reduction sharply increases the reaction rate.

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The temperature rises rapidly in the center of the reactor owing to the focal course of the reaction and inadequate participation of heat, with the result that strong vaporization of the sodium begins. The sodium vapor penetrates through pores of the titanium crust that has formed and interacts with the titanium chlorides.

The surfaces of previously formed titanium particles present active centers on which the reduction reaction of the titanium chlorides is activated, and which act as nuclei for the development of titanium concretions. In all cases, the crystallization front of the reaction products is directed upward from the original fused-sodium level.

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As a rule, the top of the reaction mass is coated with a pyrophoric layer consisting of NaCl and lower titanium chlorides, chiefly  $TiCl_3$ .

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It has been established that the reactions take place for the most part in the condensed phase at temperatures up to 500-600°C. As the temperature rises to 600-700°C, gaseous-phase reactions acquire significance, and this accelerates the process. In the 600-700°C range, mixing of the reaction mass in the reactor no longer increases the process to any marked degree, indicating that the reagents have good contact in the gaseous phase. The reaction mass obtained in the 200-700°C range contains lower titanium chlorides (chiefly  $TiCl_3$ ) and unreacted sodium in large amounts, and this greatly complicates subsequent processing of the mass and is detrimental to the quality of the metal.

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Titanium that has been reduced under these conditions takes the form of a conglomerate with sodium chloride in the form of extremely fine particles. This makes it difficult to refine the reaction mass and causes large titanium losses and deterioration of the metal's quality. The average titanium-particle size was about 3-4  $\mu m$  when the process was run in the 200-500°C range, and

about 7-8  $\mu\text{m}$  in the 500-700°C range.<sup>(2)</sup>

Temperature range from 700 to 980°C

This temperature range is of the greatest interest from the theoretical and practical standpoints. As the phase diagrams of the  $\text{TiCl}_3$ -NaCl and  $\text{TiCl}_2$ -NaCl systems indicate, readily fusible melts may appear at temperatures as low as 500-600°C. Since a melt representing a solution of Na,  $\text{TiCl}_3$ , and  $\text{TiCl}_2$  in NaCl can exist, the temperature at which the fusible melts form may be even lower.

However, because of impediments to contact between the  $\text{TiCl}_3$  and  $\text{TiCl}_2$  and the solid sodium chloride and the slowness with which they diffuse through one another, these readily fusible phases appear in the system at about 700°C.

As the phase diagrams indicate,  $\text{TiCl}_3$ ,  $\text{TiCl}_2$ , and sodium are highly soluble in NaCl in this temperature range and have high vapor pressures (see Figs. 55 and 56 and Table 30).

The appearance of a second liquid phase — the solution of lower titanium chlorides and metallic sodium in NaCl — in the heterogeneous system consisting of gaseous  $\text{TiCl}_4$ , liquid sodium, solid titanium, and NaCl, and the sharp increase in the vapor pressures of Na,  $\text{TiCl}_3$ , and  $\text{TiCl}_2$  changes the mechanism and kinetics of the reduction reactions.

Practical experience indicates that the gaseous-phase reactions are predominant: still 60-70% of the sodium placed in the reactor has been utilized, i.e., while there is a sodium excess and a relatively small amount of NaCl in the reactor. When 60-90% of the Na has been utilized, the importance of reactions in the melt increases sharply, although the gaseous-phase reactions are still significant. At more than 90% Na utilization, the reduction reactions take place for the most part in the fused salt system.

The shift of the reduction reactions from the gaseous phase into the fused salt coincides with the point at which all of the sodium left in the reactor is dissolved in NaCl. This maximum

Footnote (2) is on page 369.

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degree of sodium utilization, after which the reaction transfers to the liquid phase, can be calculated for any desired temperature. If we denote the sodium utilization coefficient by X, the residue of unused sodium is 1 - X, and the amount of NaCl formed in the process equals 2.55X, we have

$$1 - X = \frac{P_t}{100} \cdot 2.55, \quad (12)$$

$$X = \frac{1}{1 + 0.0255 \cdot P_t} \quad (13)$$

where  $P_t$  is the solubility of Na in NaCl at temperature t, in % (by mass).

Thus,  $P_t = 4.0$  (by mass) at 380°C, and the degree of sodium utilization is about 90%.

For convenience in analyzing the behavior of the reduction reactions when sodium is supplied to the reactor periodically, let us adopt a convention in which the process is divided into three characteristic periods:

1st period — up to 70% Na utilization, during which the reactions take place basically in the gaseous phase;

2nd period — at 70 to 90% Na utilization, when the reactions take place in mixed phases;

3rd period — at 90 to 100% Na utilization, when the reactions take place basically in the fused salt phase.

In the first period, as in the case of the gaseous-phase reactions at 200-700°C, the preferred reactions are the reduction of  $TiCl_4$  to  $TiCl_3$  (II') and the direct reduction of  $TiCl_4$  to Ti (I'). This trend of the reactions is explained by the high vapor pressures of  $TiCl_4$ ,  $TiCl_3$ , and sodium in the gaseous phase and by the highest kinetic probability of (I') and (II'). The extremely fine and pyrophoric titanium powder formed during this phase is deposited in considerable amounts at the top of the reactor and on its walls.

In the third period of the process, when more than 90% of the Na has been used, the entire sodium excess is dissolved in

the NaCl, and its chemical activity and vapor pressure in the gaseous phase have dropped, the principal sodium reduction reactions of the titanium chlorides are transferred into the liquid phase.

Since  $TiCl_4$  is practically insoluble in NaCl, it must be assumed that the reaction of the  $TiCl_4$  with the sodium dissolved in the NaCl takes place with formation of  $TiCl_3$  by Reaction (II') and, to some extent, with formation of  $TiCl_2$  by Reactions (III') and (IV'). During this phase, because of the high chemical activity of the titanium accumulated toward the end of the process, the reactions of  $TiCl_4$  with Ti that form  $TiCl_3$  and  $TiCl_2$  (VII', VIII') and Reactions (IX') and (X') become possible.

Since the equilibrium concentration of  $TiCl_3$  in the  $TiCl_3$ - $TiCl$ -NaCl system is several times the equilibrium  $TiCl_2$  concentration, and because of the sluggishness of the reduction of  $TiCl_2$  to Ti (V'), the reaction in which  $TiCl_3$  is reduced to Ti is developed preferentially under these conditions [271; 178, page 205; 134, page 73].<sup>(3)</sup>

During the same period, the high liquid-phase concentrations of  $TiCl_3$  and then  $TiCl_2$ , development of the active titanium surface, and the decrease in the activity of the sodium in the melt may cause the reactions of  $TiCl_3$  and  $TiCl_2$  with metallic titanium and one another. Thus, during this phase, the titanium is reduced in the fused-salt system by the stepwise reactions:  $TiCl_4 + TiCl_3 \rightarrow Ti$  (II', VI'). The presence of compounds of the type  $2NaCl \cdot TiCl_3$  [82],  $NaCl \cdot TiCl_2$ ,  $2NaCl \cdot TiCl_2$  [265],  $13NaCl \cdot 3TiCl_3 \cdot 2TiCl_2$  [106, page 60] in the fused-salt system inhibits the secondary reactions, and this favors process rate and metal quality.

The second period of the process (at 70 to 90% Na utilization) takes place in the mixed phases and is intermediate between the first and third periods. The nature and mechanism of the reactions taking place in the gaseous and condensed phases is the same here as in the first and third periods. As Na utilization increases from 70 to 90%, the importance of gaseous-phase reactions falls off, and reactions in the melt become more important. Footnote (3) is on page 369.

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Under real conditions, conditions of constant temperature, pressure, and concentration do not prevail in the reactor, and the process unfolds in a broad range of zonal temperatures, pressures, and concentrations of the reactants and the reaction products.

Systematic scaled-up laboratory investigations of the sodium reduction of  $TiCl_4$  were conducted by V.A. Shubin and V.A. Pazukhin.<sup>(4)</sup>

In the experiments, the reaction vessel holding the sodium, the floor of which was made of pressed titanium powder, was placed in the process space under the cover of the reactor. On melting, the sodium penetrated through the porous floor and reacted with  $TiCl_4$  vapor fed into the reactor.

A salt melt consisting of NaCl and  $TiCl_3$  was obtained as a result of the reactions at temperatures around 700-750°C. The NaCl: $TiCl_3$  molar ratio was close to three and underwent practically no change as the  $TiCl_4$  supply rate was reduced to a fraction. The molar ratio of the reduced metallic titanium to the  $TiCl_3$  in the melt was approximately two.

On the basis of these tests, the authors concluded that two reaction steps take place simultaneously around 700-750°C and can be described over-all by the equation



In experiments run at 800°C, the fused-out salt contained, in addition to  $TiCl_3$ , a certain amount of  $TiCl_2$ , the content of which was higher the lower the  $TiCl_4$  supply rate to the reactor. As the layer of titanium sponge grew and the time of contact between the titanium and the melt increased, the melt became appreciably poorer in  $TiCl_3$  and  $TiCl_2$ .

On the basis of the experimental data, V.A. Shubin and V.A. Pazukhin conclude that a chloride melt consisting of NaCl and  $TiCl_3$  is first to form in the reduction of  $TiCl_4$  to Ti. Like the sodium, this easily fusible melt thoroughly wets the titanium concretions, forming a continuously replenished  $TiCl_3$ - and Na-

Footnote (4) is on page 369.

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containing film on them. The titanium surface acts as a catalyst for the film reduction of  $TiCl_3$  by sodium and serves as a base for aggregation of the reduced titanium particles.

This reaction mechanism is confirmed by the experiments of S.V. Ogurtsov, who established that the reaction between Ti and  $TiCl_4$  in the presence of the NaCl coating the titanium surface proceeds at a higher rate than when Ti and  $TiCl_4$  interact without NaCl. The author explains this phenomenon as due to stepwise reduction of  $TiCl_4$  via  $TiCl_3$  to titanium in the melt [106, page 41].

Increasing the temperature and holding time of the reaction mass reduced the fraction of  $TiCl_3$  and increased those of metallic titanium and  $TiCl_2$ . As holding continues, the  $TiCl_3$  vanishes first from the reaction products, followed by the  $TiCl_2$ . This confirms the stepwise nature of the reduction reaction. The longer persistence of  $TiCl_2$  in the melt indicates that the rate of its reduction is considerably lower than that of  $TiCl_3$ , and this limits the rate of the over-all reduction of  $TiCl_4$  to the metal via  $TiCl_2$ .

V.A. Shubin and V.A. Pazukhin also established that the average particle size of the reduced titanium was 7-9  $\mu m$  at about 700°C, but decreased to 5.5  $\mu m$  at 800°C. The authors explain the irregularity of grain growth in the 700-800°C temperature range as due to the rapid development of the gaseous-phase reactions during this period.

On an increase in the argon pressure in the reactor, the gaseous-phase reactions are suppressed, with the result that the titanium particles grow rapidly. At a reactor argon pressure of about 380 mm Hg, most of the titanium was obtained in the form of dense aggregates up to 25 mm across with 80-85% titanium contents and an average density of 2.0  $g/cm^3$ .

It was also found that with a deficiency of sodium, the reduction reactions of the lower chlorides proceed basically in melt on the surface of the titanium grains, with a favorable effect on grain growth; an excess of the reducing agent, on the other hand, tends to reduce titanium-particle size.

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V.A. Shubin and V.A. Pazukhin determined the temperature variation of the rate constant of Reaction (I):

$$2.303 \lg K = \frac{1190}{T} + 1.17, \quad (14)$$

which gives a calculated activation energy of

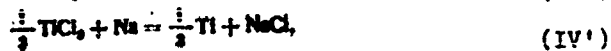
$$E = 2360 \quad (15)$$

The low activation-energy value indicates that the reduction reactions are autocatalytic in nature. Yochizawa cites a higher activation-energy value, 6040 cal/mole [273], and V.D. Savin and V.A. Peznichenko submit data indicating that it lies between 5900 to 1500 cal/mole below 800°C [287].

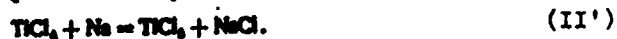
To summarize what we have said regarding the chemical mechanism and kinetics of the reactions in which titanium chlorides are reduced by sodium admitted periodically to the reactor and the mechanism of the reduction process and the aggregation of the reduced titanium particles:

1. Titanium tetrachloride and the lower chlorides of titanium begin to react with sodium at an appreciable rate at a temperature above 200°C.

2. When the process is run in the 200-700°C temperature range, the most probable reduction reactions are those between the  $TiCl_4$  vapor and the sodium and lower titanium chlorides in the condensed phase:



and the preferential gaseous-phase reactions are:



The importance of the gaseous-phase reactions increases above 600°C. The reduction of  $TiCl_2$  to titanium (V') is sluggish, especially at lower temperatures, and hence insignificant in the temperature range under consideration.

3. The process run in the 200-700°C temperature range has the following distinctive features:

a) a relatively low rate of the process and a low sodium utilization factor (about 60-70%);

b) a low degree of reduction of the titanium tetrachloride to the metal, resulting in a reaction mass with a high content of lower titanium chlorides, chiefly  $TiCl_3$ ; subsequent processing of this reaction mass is much more difficult and attended by loss of a large amount of titanium;

c) the formation of small (7-9  $\mu m$ ) titanium particles, which are closely conglomerated with sodium chloride;

d) to some extent, the reaction rate and the utilization coefficients of the sodium and titanium tetrachloride can be increased by stirring the reaction mass during the reduction.

A second liquid phase representing low-melting solutions of sodium and the trichloride and dichloride of titanium in sodium chloride may make its appearance in a heterogeneous system with the liquid sodium at temperatures above 700°C. Chemical compounds of the type  $3NaCl \cdot TiCl_3$ ,  $NaCl \cdot TiCl_2$ ,  $2NaCl \cdot TiCl_2$ , and  $13NaCl \cdot 3TiCl_3 \cdot 2TiCl_2$  have been identified in such systems.

The appearance of low-melting solutions increases the reaction rate and the importance of the reactions taking place in the salt melt; in turn, this increases the sizes of the metallic-titanium particles and aggregates and, consequently, improves the quality of the titanium.

When reductions are carried out in the 700-980°C temperature range and the sodium is utilized up to 70% (first period), the gaseous-phase reactions, chief among which are (II') and (I') take precedence.

When the reduction process is conducted in the 700-980°C temperature range and more than 90% of the sodium has been utilized (third period), the principal reactions take place in the salt melt. The stepwise titanium reduction reactions (II') and (VI') predominate during this phase.

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The reduction of  $TiCl_2$  to titanium (V) is slow and of no appreciable importance under these conditions, although the formation of titanium dichloride is more probable under these conditions than it is in the 200-700°C range.

When reduction processes are run in the 700-980°C temperature range and 70 to 90% of the Na has been utilized (second period), the reactions are mixed-phase, with the nature and mechanism of the reactions taking place in the gaseous and condensed phases analogous to those of the first and second period reactions for the corresponding phases. As Na utilization advances from 70 to 90%, the gaseous-phase reactions become less important and those in the fused salt come to the fore.

When the process is run in the 700-980°C temperature range, its rate is very high and limited, as far as is known, solely by the rate at which heat is withdrawn from the reactor. The sodium utilization coefficient reaches 100%. However, continuing the reduction to total utilization of the sodium requires very precise batching of the reactants, since the reaction mass will otherwise contain lower titanium chlorides or metallic sodium and become extremely difficult to process.

Metal particles with sizes of 5-6  $\mu m$  are produced in the 700-980°C temperature range and aggregate into larger concretions on the surface of the previously reduced titanium. Increasing the reaction-mass holding time and temperature at the end of the process or increasing the argon pressure in the reactor results in an increase in the titanium-concretion sizes to 10-25 mm.

Discussion of the reactions in a certain temperature range or during a certain period is somewhat arbitrary, since the reactions proceed zonally. The large exothermic heat effects of the reactions and nonuniform dissipation of heat from the reactor result in large temperature, pressure, and reactant-concentration gradients in the working space, with the result that gaseous-, liquid-, and solid-phase reactions take place simultaneously in the reactor with secondary and disproportionation reactions.

What we have said regarding the mechanism of the sodiothermic  $TiCl_4$  reduction applies for periodic delivery of sodium to the reactor. With simultaneous, continuous delivery of the  $TiCl_4$  and Na into the reactor at 700-980°C in the proportions stoichiometric for Reaction (I'), they react at such a high rate that the stepwise nature of the reactions is practically effaced. On the other hand, lower titanium chlorides form on a departure from stoichiometric  $TiCl_4$  and Na proportions when they are fed into the reactor simultaneously and continuously. Thus, at  $TiCl_4:Na = 1:1$ , the principal product is titanium trichloride, while the dichloride forms preferentially at the proportions  $TiCl_4:Na = 1:2$ .

#### Design of Equipment and Process Technology

The reduction of titanium tetrachloride by sodium is accompanied by the release of a large amount of heat. The enthalpy of the over-all reaction



is 204.4 kcal/g-atom of titanium under standard conditions and exceeds the enthalpy of the magnesiothermic reduction by 66%. The amount of heat released in modern reactors for the sodiothermic reduction of  $TiCl_4$  is about 450-600 thousand kcal/h. A considerable part of this heat must be withdrawn from the reactor to maintain the desired set of conditions.

The industrial technology of the sodiothermic titanium reduction is based on a process run in the 750-980°C temperature range with simultaneous delivery of liquid sodium and titanium tetrachloride into the reactor in near-stoichiometric proportions.

Figures 57-60 present a schematic drawing and photographs of a reactor used for the sodiothermic reduction of titanium at the Ashtabula plant of the American firm Electrometallurgical. The reactor is 1500 mm in diameter and 4300 mm high. It is made of stainless steel with an inner lining of low-carbon steel. The total thickness of the reactor wall is 25.4 mm [245]. The expensive two-layered steel is used in an effort to prolong reactor service life, which is limited at high temperatures chiefly by

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the scaling resistance of the material of which the reactor outer surface is made. Everything said earlier regarding selection of materials for magnesiothermic reactors also applies to the materials that may be used for construction of a sodiothermic reactor.

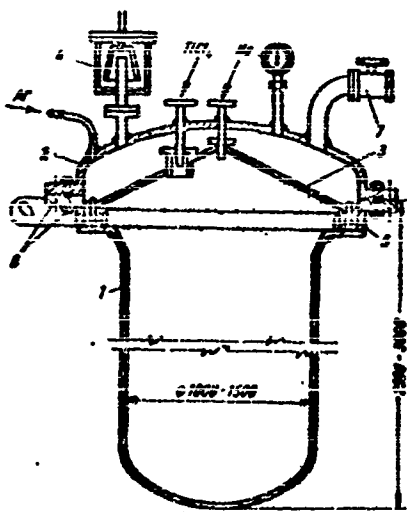


Figure 57. Diagram of reactor for sodiothermic reduction of  $TiCl_4$ . 1) Reactor casing; 2) reactor cover; 3) shield; 4) slidevalve unit; 5) salt lock; 6) runners for cooling flanges; 7) connection for evacuating reactor.

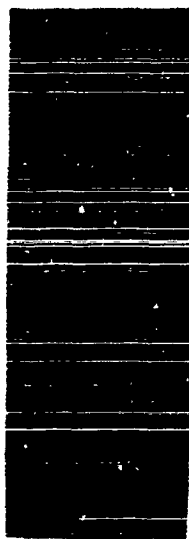


Figure 58. Reactor for sodium reduction of  $TiCl_4$ .

The dome-shaped cover of the reactor has a connecting pipe for evacuation of the reactor and filling it with argon,

fittings for the delivery of titanium tetrachloride and sodium into the reactor, and a connection with a slidevalve device for bleeding pressure from the reactor. A heat shield is installed under the reactor cover and usually packed with a salt lock, whose purpose is to prevent vaporized sodium, titanium tetrachloride, and lower titanium chlorides from entering the cold zone of the reactor between the shield and the cover. At the beginning of the reduction process, when there is an excess of sodium in the reactor, the heat shield also serves as a condenser, on whose surface the sodium vapor condenses and is drained into the reactor's

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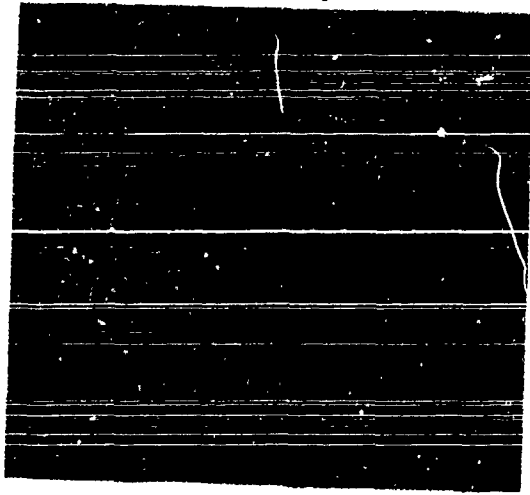


Figure 59. Service level (top) of reactor for sodium reduction of  $TiCl_4$ .

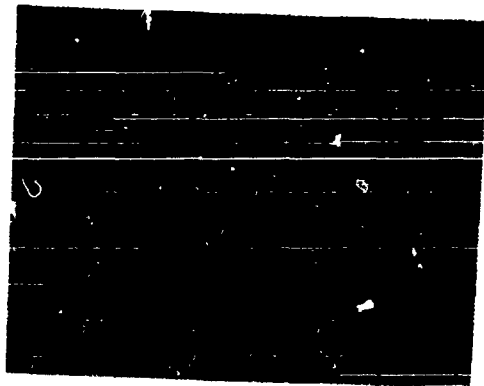


Figure 60. Service level of  $TiCl_4$  reduction department.

Unlike the reactor used in the magnesium reduction of titanium tetrachloride, this reactor does not have a device for drainage of the sodium chloride formed during the reduction, since it is not drained from the reactor either during the process or after its completion [214, 215, 245]. This is because the sodium chloride may take minute titanium particles, lower titanium chlorides, and sodium with it when it is drained. When the titanium particles, lower chlorides, and

working source.

The cover and casing of the reactor are packed with gaskets made of vacuum rubber, graphitized asbestos, or copper or aluminum wire, or by welding [245]. When vacuum rubber is used, the flanges are cooled with oil or water fed into runners on the cover and reactor flanges.

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sodium present in the drained sodium chloride come into contact with atmospheric air, they oxidize vigorously, with the resulting substantial titanium losses. This process releases large amounts of heat and gases, to the detriment of working conditions and the safety of operating personnel. Moreover, in the sodium reduction of  $TiCl_4$ , the fused sodium chloride is a process atmosphere that favors stabilization of the reduction process and improves conditions for crystallization of the titanium.

These are the reasons why the sodium chloride is not drained during the sodiothermic reduction of titanium tetrachloride. From the standpoint of reactor useful-volume utilization, this is a deficiency of the technology under discussion, since there are about 2.7 liters of NaCl per liter of reactor volume occupied by reduced titanium, which has a mass per unit volume of about 2 kg/liter.

Furnace designs for the sodium reduction of  $TiCl_4$  are similar to those used in the magnesiothermic process. Since the amount of heat released in a sodiothermic reactor is 2-3 times the amount in the magnesium process owing to the larger exothermic heat effects of the reactions and the higher rate of the process, the cooling systems used in furnaces of the former type must be more efficient.

The problem of heat offtake from a sodiothermic reactor is more complex than for the magnesiothermic process. To a certain degree, the situation is made easier by the fact that, in contrast to the magnesiothermic process, the peculiarities of the sodium process make it possible to switch off the bottom zone of the furnace after the reactor has been warmed up and the reduction reaction has begun in it, since it is unnecessary to drain the sodium chloride produced and there is no danger that the reducing agent and the lines through which it is transported into the reaction zone will freeze. Furthermore, the larger capacity of a sodiothermic reactor as compared to a magnesiothermic reactor with the same per-cycle output gives it a larger surface area and hence promotes dissipation of heat.

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In addition, vaporization of the sodium in the reaction zone and its condensation in the reactor's cold zones during the reduction of  $TiCl_4$  with a sodium excess creates conditions favoring uniform temperature distribution in the gas space and transfer of heat into the cold zones of the reactor; in combination with the progress of reduction reactions in the fused salts, this equalizes temperatures in the reactor and permits cooling it more efficiently.

The relatively uniform evolution of heat in the sodiothermic reactor, especially after the process rate has stabilized, makes it possible to dispense with thermocouples in the reactor working space and measure temperature with external temperature senders at the most characteristic points on the surface of the unit. This simplifies reactor design.

In certain cases, it is necessary to measure the temperature of the shield under the reactor cover. This is most frequently the case during the initial phase of the process, when heat transfer to the shield increases sharply owing to condensation of sodium vaporized in the reaction zone onto the shield. In this case, a temperature sender is mounted on the reactor shield and the indication used to regulate the rate of delivery of titanium tetrachloride into the reactor.

Precision batching of the  $TiCl_4$  and sodium that are fed into the reactor simultaneously during this process is a particularly complex task, in which a  $\pm 0.5\%$  deviation from stoichiometry is regarded as acceptable. Wrong proportioning of the  $TiCl_4$  and sodium disturbs the process and results in a reaction mass saturated with lower titanium chlorides or sodium. Refinement of such a reaction mass is extremely difficult, a large amount of titanium is lost, and the quality of the metal deteriorates sharply.

The sodium flowrate is usually measured with electromagnetic flow meters. The principle is measurement of the electromotive force that arises in the sodium stream crossing the field of a special magnet. Sodium delivery is regulated with needle-bellows vacuum valves, which are usually made from stainless steel, as are

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all pipelines and containers in contact with the molten sodium. The flowrates and proportions of the  $TiCl_4$  and Na are programmed by a special device and regulated automatically. The control parameters used to guide the reduction process are the temperature and pressure in the reactor at a given flowrate and the proportions of titanium tetrachloride and sodium.

Before placing it in the furnace, the assembled reactor is carefully sealed and evacuated to a residual pressure of 200-300  $\mu$ m, followed by leak-testing. A reactor in which the loss of vacuum during this test does not exceed 5-8  $\mu$ m/min is regarded as tight.

The sealed reactor is installed in the furnace, evacuated again to a residual pressure of 200-300  $\mu$ m, and then supplied with purified argon to an excess pressure of 0.2-0.3 atm. The reactor is heated with the argon to 500-600°C, the argon pressure in it is lowered to 40-80 mm Hg, and delivery of the starting reactants is begun. For a few minutes at the start of the process, the reactor receives only liquid sodium; the object here is to stabilize sodium flowrate and test the monitoring and measurement instruments and the automatic systems. Simultaneous delivery of the  $TiCl_4$  with the sodium into the reactor is then started, with observance of stoichiometric proportions.

At the beginning of the process, when the volume of reaction mass is still small and there is no sodium excess in the reactor, the highest temperatures are observed at the base of the reactor. Then, as a result of development of the gaseous-phase reactions, the maximum-temperature zone shifts to the top of the reactor and remains there until 60-75% of the sodium has been utilized. During this period, much of the heat can be taken off through the reactor cover, and the shield temperature is the basic parameter with reference to which the rate of the reduction process can be regulated.

Experiments run with periodic sodium loading have indicated that the temperature at the top of the reactor rises sharply immediately after injection of a portion of sodium into it; this

indicates rapid vaporization of the sodium and progress of the reduction reactions in the gaseous phase.

After consumption of 60-75% of the Na, the maximum-temperature zone gradually migrates to the middle of the reactor, indicating deceleration of the gaseous-phase reactions and a shift of the reactions to the surface of the melt and into it.

On utilization of more than 90% of the sodium, the maximum-temperature zone is entirely within the melt, where it remains to the end of the process; this indicates vigorous progress of the reactions in the fused NaCl. The process rate remains high.

Under industrial conditions, an effort is made to conduct reduction with a small (1-3%) sodium excess in order to prevent formation of lower titanium chlorides. At the end of the process, sodium delivery is cut off, and the supply of titanium tetrachloride is continued at a slow rate until the sodium is 100% utilized.

The average rate of titanium chloride delivery over the reduction time is about 450-600 kg/h. In the initial phase, until 10-15% of the sodium is utilized, the delivery rate is held at the 200-400 kg/h level, then raised to 500-700 kg/h, lowered again at 98-99% sodium utilization, and held at the 40-60 kg/h level until all of the sodium has been utilized.

On termination of titanium tetrachloride delivery, the furnace electric heat is switched on and the temperature in the reactor is raised to 960-1000°C. The temperature is held at this level for 4-6 h, during which time the lower chlorides are reduced and, in the opinion of some authors, the reduced titanium particles increase in size [245].

After the high-temperature hold, the electric heaters are switched off and the reactor is cooled in the furnace to 600-700°C to prevent oxidation of the reactor material when it is extracted from the furnace. Cooling of the reactor in the furnace takes 2-4 hours, after which it is transferred to a chilling platform for forced air cooling to lower its temperature further [214, 215]. On cooling to the ambient temperature, the reactor is transferred

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Smolinsky tested a variety of ways of delivering the titanium tetrachloride and sodium into the reactor [252]. They included:

a) injection of the titanium tetrachloride into a layer of fused sodium and potassium chlorides with liquid sodium on its surface;

b) introduction of liquid sodium into a layer of fused sodium and potassium chlorides under titanium tetrachloride vapor in the reactor's gas space;

c) introduction of sodium and titanium tetrachloride simultaneously into the fused sodium and potassium chlorides.

It was found difficult in all cases to prevent buildups in the orifices of the feeders through which sodium or  $TiCl_4$  was delivered into the fused salt. Further, vigorous agitation of the fused bath produces an extremely fine titanium powder. A certain amount of interest attaches to solution of the metallic sodium in the fused salt before the  $TiCl_4$  is delivered into the reactor. In this case, the reaction rate is quite high and the titanium is produced in the form of larger particles that are easily separated from the salt.

At the present time, however, the most highly perfected and practically useful industrial method is that in which the titanium tetrachloride vapor and liquid sodium are delivered simultaneously into the reactor gas space in near-stoichiometric proportions.

Below we shall consider the equipment and technology used at the Ashtabula plant of the American firm Electrometallurgical as a working industrial example of the sodiothermic process [214, 215, 245]. The reduction reactors, the design of which was discussed above, are installed in a resistance furnace 2400 mm in diameter and 6100 mm high. There are 24 reduction units, with 12 accommodated in each of two plant buildings. Two metering tanks are installed in each furnace: a 1.8-2.2-ton tank for sodium and a 3.6-4.5-ton tank for the titanium tetrachloride. The reduction cycle begins with evacuation of the reactor to a residual pressure

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of 300  $\mu\text{m}$  Hg by means of a four-stage vapor-ejection pump. The reactor is then filled with argon and installed in the furnace. Sodium and  $\text{TiCl}_4$  are delivered simultaneously into the reactor for 5-7 h. Then the furnace is switched on, the reactor heated to  $1000^\circ\text{C}$ , and held at that temperature for 4-6 h to complete the reduction reaction. Then the furnace heaters are switched off and the reactor is cooled in the furnace for 2 to 4 h.

For further cooling, the reactor is placed on a chilling platform, where cold air is blown over it. Air heated in this manner is used to heat the plant during the winter.

It is easily seen from the above figures that the per-cycle output of the reactor is about 1000 kg of titanium in this case, and that the average hourly flowrate of titanium tetrachloride ranges from 600 to 850 kg or  $35\text{-}50\text{ g/cm}^2$  of reactor cross section. The equipment is tied up for a total of about 12-18 hours in a single reduction cycle.

Published technical literature offers practically no data on the influence of temperature, pressure, and titanium tetrachloride flowrate on the course of the reduction processes carried out in industrial reactors or on the quality of the titanium produced.

V.A. Shubin and V.A. Pazukhin,<sup>(5)</sup> S.V. Ogurtsov and V.A. Raznichenko [106, page 60], V.D. Savin [287], and others have studied the influence of these factors under laboratory conditions. The optimum established was utilization of the titanium tetrachloride and sodium to practically 100% of the stoichiometric quantities. In all experiments, increasing the rate of titanium tetrachloride delivery into the reactor and raising the temperature from 800 to  $960\text{-}1000^\circ\text{C}$  resulted in larger titanium particles and aggregates. Increasing the argon pressure in the reactor had a similar effect.

Certain aspects of temperature variation were studied by A.I. Voynitskiy et al. [251] during reduction of  $\text{TiCl}_4$  by sodium in an industrial-type reactor. The  $\text{TiCl}_4$  was delivered into the reactor continuously at a high rate, but the sodium was fed in periodically after 95-98% of the preceding portion had been consumed. The highest temperature develops above melt level. After 60-75%

Footnote (5) is on page 369.

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of the reducing agent had been utilized, the maximum-temperature zone shifted into the melt because of the development of reactions between the titanium chlorides and the sodium dissolved in the salt. The differences between the readings of thermocouples placed at the same level in the melt were very small, indicating that the reactions were advancing throughout the entire volume of the salt, and not zonally. It was established that delivery of  $TiCl_4$  and sodium into the reactor simultaneously in such a way that reducing-agent utilization will be above 95% at all times is most expedient. This minimizes the importance of gaseous-phase reactions, so that the process can be accelerated and larger particles of high-grade metal can be produced.

A.I. Voynitskiy and O.V. Perfil'yev also established that the insignificant difference between the melting point of sodium chloride and the boiling point of sodium ( $82^\circ C$ ) does not present any major difficulties in the sodiothermic process, as had been assumed at one time [245]. Running the process in the  $801-883^\circ C$  range results in vigorous evaporation of the sodium, which is accompanied by expenditure of about 1000 kcal per gram-atom of sodium. The sodium vapor condenses in the top of the reactor, so that heat is withdrawn rapidly from the working zone. To a substantial degree, the reaction proceeds simultaneously in the gaseous phase and is accompanied by evolution of large amounts of heat; this is a characteristic aspect of the sodiothermic process run with a small sodium excess [92, 104, 160, 209, 210, 217, 223].

#### Preparation of Sodium for Reduction Process

Metallic sodium is now produced by electrolysis of alkali solutions or sodium chloride. Thermal methods of producing sodium have not yet been used to any appreciable degree in industry [232, 234]. Most of the sodium used to reduce titanium is produced by electrolysis of fused sodium chloride. The raw material for sodium production in this case is relatively uncontaminated sodium chloride produced during the reduction of titanium tetrachloride by sodium.

Currently, sodium chloride is electrolyzed in Downs electrolyzers at 580°C, amperages of 25,000-40,000 A, and a voltage of 7.0 V. The unit-current sodium yield is 80-85% and the rate of electric power consumption about 11,000 kW·h/ton of Na [242].

With practically 100% sodium utilization and 95% extraction of commercial titanium from the  $TiCl_4$ , 1.82 kg of Na must be used to produce 1 kg of titanium. In magnesiothermic reduction, the amount of magnesium used per kg of titanium is 1.24 kg, figuring with 70% magnesium utilization and a 95% yield of commercial titanium from the  $TiCl_4$ . A kilogram of Na costs about 40 cents, and a kilogram of magnesium about 80 cents. Thus, the cost of the reducing agent in the sodiothermic method is about 78 cents per kilogram of titanium, as against 99 cents, or 25% more, in the magnesiothermic process. The calculation is made for American conditions; elsewhere, this relationship might be tipped slightly in favor of magnesium. However, given well-developed sodium and sodiothermic-titanium industries, the cost of the sodium per kilogram of reduced titanium may be held below the cost of magnesium.

The amount of electric power used in producing the sodium needed to reduce 1 kg of titanium is about 20 kW·h, as against about 21.5 kW·h when magnesium is used.

Acquisition of sodium of high purity is made easier by the fact that sodium chloride is usually electrolyzed in an inert atmosphere to prevent oxidation of the sodium. There are two methods for subsequent purification of the sodium: distillation or filtration, and they both yield metal of high purity.

The contents of the principal impurities in sodium produced in Great Britain and purified by filtration or distillation are as follows: less than 0.001% each of calcium, magnesium, silicon, and nickel, 0.006% oxygen, 0.0005% iron [242].

Distillation of sodium, which has a relatively low boiling point (883°C) can be used to produce 99.99% pure metal in which the oxygen content does not exceed 0.006% and nitrogen is practically absent [236]. Purification of sodium by distillation is made easier by the fact that, even at high temperatures, sodium

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has practically no reaction with the structural materials of which the equipment and pipelines in contact with the sodium are made — primarily iron, nickel, and copper.

However, the purification of sodium by distillation requires a large amount of power and is very expensive. Distillation requires 3.0 kW·h per kg of sodium. Filtration is a simpler and less expensive method of purifying sodium and usually yields a product at least as good as the distilled metal.

Sodium is usually filtered through a layer of fine metal screens and porous cermet filters. It has been established that glass is a good adsorbent for sodium oxide, and for this reason sodium is sometimes filtered through a bed of glass powder [237]. Satisfactory results are obtained by filtering sodium through material with a pore size of about 5  $\mu$ m [238].

During filtration, the sodium is cleared of iron, calcium, oxide, nitride, and sulfate impurities. The solubility of sodium oxide in the metal declines as the temperature of the metal decreases. Thus, it is 0.023–0.027% in the 100–150°C range (or 0.006–0.007% after conversion to oxygen), and increases by a factor of 2–3 at 200°C [239]. For this reason, sodium must be filtered at the lowest possible temperatures. The temperature used in practice range from 110 to 120°C.

At the Ashtabula plant, sodium is filtered through 20 layers of screening with hole diameters of about 40  $\mu$ m and a perforated steel plate with a hole diameter of 20  $\mu$ m [240]. Since it is necessary to clean the filters periodically to remove the accumulated oxides, two units are set up in parallel — one operating and one being cleaned.

To prevent sodium oxide from building up on the filtering screens and plates, it is recommended that the work be done with the screens and plates covered at all times by a layer of metal and that the entire system be filled with an inert gas. To remove suspended matter from the screens, pure metal is forced back through them; as a rule, the basic direction of filtration is from bottom to top. The filter is washed by feeding metal down

through it. In this case, suspensions are easily removed from the filter and drop into a collector from which they are periodically removed.

Since sodium production has recently developed into the large tonnages and sodium has come into extensive use in the chemical, nuclear-power and electrical industries, its storage and long-distance shipment, including piping of liquid sodium, are functions that have been rather well developed from the design and technological standpoints and present no major technical difficulties.

The shipment of metallic sodium in 36-ton railway tank cars with internal oil-heated coils to warm the metal before it is drained and dry the tanks before filling has been described [240]. When the metal is being warmed, the oil temperature is held at about 120°C. After the sodium has been melted in the tank, argon pressure is applied (~1.0 atm) and the sodium is displaced into intermediate storage tanks at the sodium-using plant. Under ordinary conditions, sodium is stored under a layer of oil or kerosene. To prevent carbon contamination, sodium to be used in reducing titanium is usually stored under argon.

Sodium can be transferred by displacement with an inert gas, with centrifugal or electromagnetic pumps, or by vacuum suction. The latter method is preferred, since sodium is highly fluid at 120°C and penetrates through any defective seals in pipelines and equipment of a pressurized system. In the vacuum-transfer method, sodium does not escape through defective seals in the system, since this is prevented by suction of air through the defect and oxidation of the metal at this point, so that the oxide plugs the leak. Barometric traps are installed to prevent sodium from entering the vacuum system of the pumps [241].

At the Electrometallurgical Ashtabula plant, the pipeline used to transfer sodium from railway tank cars to the reduction reactors is 1200 meters long, the lines are induction-heated, and magnesium oxide provides heat insulation. According to data obtained in practice, the power required for electric heating of one meter of sodium-filled pipeline 50 mm in diameter is 100 W

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for induction heating and 75 W for wire-coil heating [44].

A major disadvantage of sodium is its high chemical activity, which requires extremely careful design and observance of special precautionary measures.

Safety measures for work with sodium are set forth in detail in the specialized literature [242-244]. We note, however, that the reaction of metallic sodium with water is particularly dangerous, since it proceeds with vigorous evolution of hydrogen and heat and is consequently explosive. Hence all necessary measures must be taken to exclude the possibility of the sodium-water reaction. Use of water in the same areas with sodium, including its use to cool equipment holding sodium, is strictly prohibited. Metallic sodium also reacts vigorously with chlorinated hydrocarbons (for example,  $\text{CCl}_4$ ) and dry ice.

The sodiothermic reduction of titanium produces a certain amount of wastes that contain unreacted sodium and must be rendered harmless. It is recommended that they be generously doused with kerosene, ground up, and burned for this purpose [242], or else treated with sodium hydroxide solution with thorough removal of the hydrogen formed in the process to prevent formation of explosive mixtures.<sup>(6)</sup>

#### Two-Stage Reduction

As we noted above, the lower titanium chlorides formed in the sodium reduction of  $\text{TiCl}_4$  are readily soluble in fused sodium chloride. As a result, low-melting eutectics form in the salt phase, along with chemical compounds of the types  $\text{NaCl} \cdot \text{TiCl}_2$ ,  $2\text{NaCl} \cdot \text{TiCl}_2$ ,  $3\text{NaCl} \cdot \text{TiCl}_3$ ,  $13\text{NaCl} \cdot 3\text{TiCl}_3 \cdot 2\text{TiCl}_2$  etc. [106, page 60; 259; 262; 265, 266].

The presence of these low-melting eutectics and chemical compounds in this system, together with the high solubility of metallic sodium in  $\text{NaCl}$ , make it possible to carry out the reduction process in two stages.

The first stage of the process is run at 500-800°C under conditions such that the reduction proceeds not to metallic titanium, Footnote (6) is on page 369.

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but to its lower chlorides. This is accomplished by conducting the process with less than the stoichiometric amount of sodium. As a rule, the process is carried to formation of  $TiCl_2$  or to the binary and ternary salts mentioned above. In the first step of the process, i.e., the reduction of  $TiCl_4$  to the lower chlorides, about 60% of the total heat of the reduction reaction of  $TiCl_4$  to the metal is released. The reactions that reduce  $TiCl_4$  to the lower chlorides proceed at high rates and permit the design of highly productive reactors for the first stage of the process. Here it is important not to permit the reduction of  $TiCl_4$  to titanium in the gaseous phase or disproportionation reactions to advance to any marked degree, since a large amount of finely dispersed titanium would then form in the reactor and not only lower the yield of high-grade metal from the  $TiCl_4$ , but also complicate the second process stage in which the lower chlorides are reduced to titanium. At the same time, the formation of a small amount of finely dispersed titanium during the first stage is even desirable, since it absorbs a substantial amount of impurities and this makes it possible to obtain purer metal in the second stage.

In the second stage of the process, the lower titanium chlorides, which are dissolved in sodium chloride, are reduced by sodium fed onto the melt surface. The reactions are diffusive in nature.

The resulting titanium particles are then nuclei on whose surfaces large titanium crystals grow, reaching lengths up to 25-100 mm and thicknesses of 3-8 mm. During the second stage of the process, the reduction proceeds quite rapidly at 600-1000°C, releasing about 40% of the heat of the over-all reduction of  $TiCl_4$  to titanium. It is especially advantageous to reduce binary titanium salts and the so-called "black salt" ( $13NaCl \cdot 3TiCl_3 \cdot 2TiCl_2$ ) since this minimizes the disproportionation reactions, which produce finely dispersed low-grade titanium [266].

Two-stage sodium reduction of  $TiCl_4$  can produce titanium of very high purity, with quality approaching that of iodide titanium. It has been reported that this method has produced metal

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with hardnesses of 60-80 HB [106, page 60; 246].<sup>(7)</sup> Obviously, the acquisition of high-grade titanium is related not only to peculiarities of the reduction process itself, but primarily to peculiarities of the crystallization of titanium in large crystals that do not contain interstitial elements in their lattices and have small specific surface areas and, consequently, low surface activities. This reduces the adsorption of contaminating gases on the surface of the metal and, with it, the amounts of impurities in the titanium ingots melted out of these crystals.

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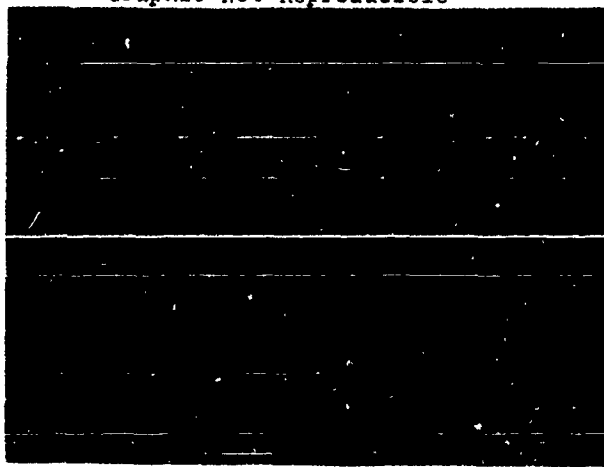


Figure 61. Titanium crystals obtained by reducing  $TiCl_4$  with sodium in two stages.

Figure 61 shows titanium crystals obtained by the two-stage sodiothermic method.

It has been found that slowing sodium delivery in the second stage and dilution of the fused lower chlorides with sodium chloride promotes crystal growth.

In addition to improving quality, the two-stage reduction, in which 60% of the net heat effect is released in the first stage and 40% in the second stage, and in which there is no appreciable bonding of the titanium crystals to the reactor walls, creates

Footnote (7) is on page 369.

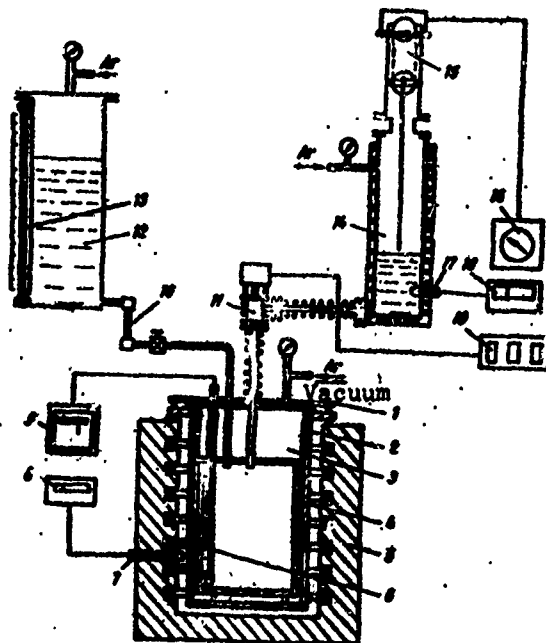


Figure 62. Diagram of installation for two-stage reduction of  $TiCl_4$  by sodium.

- 1) Retort cover; 2) retort; 3) shield;
- 4) inner shell; 5) furnace; 6) three-point thermocouple; 7) external thermocouple; 8) contact galvanometer; 9) potentiometer; 10) rotameter; 11) bellows valve; 12)  $TiCl_4$  tank; 13) level tube;
- 14) sodium tank; 15-16) automatic controller; 17) thermocouple for temperature measurement in sodium tank; 18) contact galvanometer; 19) timing relay.

conditions favorable for semicontinuous and continuous processes for the sodium reduction of  $TiCl_4$ .

Figure 62 presents a schematic diagram of a two-stage installation for the sodium reduction of  $TiCl_4$ . The  $TiCl_4$  is reduced first to the lower chlorides and then, in the second stage, to titanium in the same reactor.

Several variants of the two-stage process have been proposed. Thus, Schott and Hansley [246] recommend temperatures of 150-400°C

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for the first stage, with introduction of 25 to 90% of the stoichiometric amount of Na into the reactor to reduce the  $TiCl_4$  to the metal. The second stage is run at 805-1050°C with addition of sodium in the amount necessary for complete reduction of the titanium. The rate of injection of sodium into the reactor during the second stage determines the size and structure of the crystals and blocks of the resulting metal. As a rule, rapid introduction of the sodium produces fine-grained titanium, while large crystals form preferentially at low sodium feed rates. The titanium produced has hardnesses of 60-70 HB. It is recommended that the reaction mixture be transferred from the first, low-temperature reactor into the fused salt bath of the second reactor by worm feed; the entire system must be airtight.

Keller indicates that the first stage of the reduction to  $TiCl_2$  must be run at a reactor temperature above 800°C with vigorous stirring.<sup>(8)</sup> Voge [transliterated from Russian] proposes that the NaCl melt with the lower chlorides that is obtained during the first stage of the reduction be poured into a box and placed in a reduction furnace held at temperatures up to 1000°C for the second stage. The sodium is injected onto the surface of the melt at several points along the length of the box. The reduced crystals form a crust on the melt surface. Since the level of the fused salt rises during reduction, it coats this crust and the crystals grow upward in the fused salt from the original crust, reaching lengths up to 25 mm. After reduction is complete, the box is placed in a furnace so that the excess salt can be melted out.

Kingsbury<sup>(9)</sup> proposes that the first stage be run at 700°C to produce a melt containing 26.5%  $TiCl_2$ , 34.5%  $TiCl_3$ , and 39.0% NaCl which corresponds to the compound  $3NaCl \cdot TiCl_2 \cdot TiCl_3$ . After freezing, the resulting melt is crushed and loaded at 825°C into the second-stage reactor, which has been filled with sodium. Obviously, the reduction will produce some titanium granules mixed with NaCl and sodium, which it is proposed to separate in a vacuum or subject to hydrometallurgical refinement; this would be extremely difficult owing to the sodium excess in the reaction mixture.

Footnotes (8) and (9) are on page 369.

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Keller<sup>(10)</sup> proposes that the process be carried out in a reactor consisting of two parts separated by a perforated partition. The NaCl melt with the lower titanium chlorides, basically  $TiCl_2$ , would be on one side of the partition, and a sodium-saturated NaCl melt on the other. The partition would prevent mixing of the melt and localize the reduction zone. Large crystals grow on the perforated partition at 850-950°C.

This method was proposed in a different design version by V.A. Pazukhin and V.A. Shubin.<sup>(11)</sup>

To prevent the lower titanium chlorides from reacting with the reactor material, M. Glinichka proposes that the first reduction stage be run in a reactor whose walls are lined with NaCl.

Other versions of the two-stage process have also been suggested.<sup>(12)</sup> The increased frequency of patents for the two-stage process indicate that intensive research is being carried out toward the development of this promising method.

#### Reduction by Amalgams and Mixed Reducing Agents

The effort to simplify the sodiothermic method of  $TiCl_4$  reduction and make it less expensive has led to the testing of sodium amalgam as a reducing agent. Sodium amalgams can be produced easily by electrolyzing a solution of sodium chloride or hydroxide in a bath with a mercury cathode at 25-30°C.

As we know, the solubility of sodium in mercury is 0.1-0.7% at temperatures from 0 to 50°C, 1.25% at 50-100°C, and about 2.5% at 150°C. In production of the amalgam, the electric power consumption per kilogram of sodium in the amalgam is smaller by a factor of 2-3 than when metallic sodium is produced by electrolysis of used sodium chloride; consequently, the cost of the sodium in the amalgam is also substantially lower than the cost of metallic sodium [245, 247].<sup>(13)</sup>

$TiCl_4$  can be reduced to the metal not only by amalgams of sodium, but also by amalgams of calcium, potassium, and lithium. Reduction is promoted by the reaction of the titanium product with the mercury, with formation of the intermetallic compound  $TiHg$ .

Footnotes (10), (11), (12) and (13) are on pages 369 and 370.

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This releases about 7 kcal/g-atom of heat, an indication that this compound is quite stable.

The chlorides of sodium, calcium, potassium, and magnesium have melting points considerably higher than the boiling point of mercury. For effective management of the process, it is necessary that the salts that are formed be kept fused, with the mercury vapor pressure in the reactor running to several tens of atmospheres. It is therefore recommended that the reduction process be carried out with an amalgam of two metals whose chlorides form low-melting eutectics [248]. The two metallic reducing agents must have activities in the amalgam that give them approximately identical affinities for chlorine; this is necessary for their simultaneous reaction with the  $TiCl_4$  and the formation of a low-melting eutectic in the process. These requirements are nicely satisfied by amalgams of sodium with calcium, since their chlorides have a eutectic with a melting point at about 500°C.

The content of the reducing metals in the amalgam should not exceed 1-3% (by mass) so that the amalgam will remain fluid at room temperature. The reduction is usually carried out at about 520°C with a mercury vapor pressure of about 10 atm prevailing in the reactor.

The result of reduction is a mobile mass that is easily separated from the salts after they have solidified and filtered on a filter whose holes are about 20  $\mu$ m in diameter. The mercury filtrate that results contains practically no titanium, and the yield of filtrate is about 90% of the mercury originally taken. The residue on the filter is a titanium amalgam and is distilled at 700°C in an inert-gas atmosphere, leaving pure metallic titanium in the solid phase, while the mercury that has been driven off is recycled. Distillation of the mercury is a simple and inexpensive process, since it is necessary to vaporize only an insignificant part of the mercury taken for the process (about 5-6%).

It has been computed that the cost of the reducing agent amounts to no more than 0.5% of the cost of titanium in this process, while the cost of the reducer represents about 20% in the

reduction of  $TiCl_4$  with metallic sodium. An important drawback of the amalgam process is the rapid turnover of mercury, which results from the relatively low solubility of sodium and titanium in it at moderate temperatures; another is the high toxicity of mercury. These two factors render the amalgam process rather unworkable at the present time.

A process in which  $TiCl_4$  is reduced at 550-600°C by an alloy of sodium with zinc has been proposed. In the 550-600°C range, the solubility of sodium in zinc is about 2.5%, while that of titanium in zinc is 0.45%. As a result of reduction, all of the titanium is dissolved in the excess of zinc and easily separated from the salt phase after cooling. The resulting Zn-Ti alloy is filtered at 850-950°C, and the filter residue is separated into its components by vacuum distillation at 700-800°C [249].

Use of zinc instead of mercury makes it possible to eliminate the toxic mercury from the process, but sacrifices the basic advantage of the amalgam method -- use of an inexpensive reducing agent. The process requires highly purified zinc, which is very expensive. Certain improvements to the process have been suggested. (14)

The metal produced by the amalgam methods is inferior in quality to titanium obtained by the magnesio- and sodiothermic methods, and this is another disadvantage of the amalgam processes.

Some of the proposals call for a sodiothermic process run at temperatures below 800°C. As we noted earlier, the reduction of  $TiCl_4$  by sodium then proceeds with formation of the lower chlorides; the crust formed on the surface of the salt inhibits the process. However, crusting can be prevented by formation of readily fusible melts in the reactor during the reduction process, e.g., a melt of sodium and potassium chlorides ( $NaCl:KCl = 1:1$ ) with a melting point of 665°C. For this purpose, it is recommended that the appropriate amount of potassium chloride be injected into the reactor or that the process be run with an alloy of sodium with potassium as the reducing agent. (15)

Footnotes (14) and (15) are on page 370.

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Use of the sodium-potassium alloy that has a eutectic melting at  $-12^{\circ}\text{C}$  at 22.7% Na results in more favorable conditions. These two metals differ little as regards affinity for chlorine and can reduce  $\text{TiCl}_4$  simultaneously; the resulting melt is at equilibrium with an alloy of definite composition. This makes it possible to select a low-melting salt mixture, and this is what determines the composition of the alloy for reduction of the  $\text{TiCl}_4$ . However, the high cost of potassium prohibits its use in an alloy with sodium for reduction of  $\text{TiCl}_4$  if metallic potassium is used to prepare this alloy. There is a cheaper method for producing the sodium-potassium alloy: reduction of KCl by sodium. Since potassium has a somewhat higher affinity for chlorine than does sodium, the melt to be reduced must at all times have a large KCl excess in order to obtain an alloy with a high enough potassium content. Thus, at  $900^{\circ}\text{C}$ , the alloy containing 16.1% K and 83.9% Na is at equilibrium with a fused salt mixture containing 61.2% KCl and only 38.8% NaCl. A relatively cheap alloy can also be produced by electrolysis of process NaCl-KCl melt formed during reduction.

The very high chemical activity of potassium makes the entire technological process much more difficult and requires special measures to ensure safety of the operating personnel. In addition, the explosive peroxide  $\text{K}_2\text{O}_2$  forms when potassium oxidizes. Oxygen present in the potassium during reduction transfers to the titanium, to the sharp detriment of its quality. All of this makes the method rather unpromising for industrial application at the present time.

The reduction-process temperature can be lowered by using a mixture of sodium and magnesium as the reducing agent, bearing in mind that the eutectic mixture of their chlorides, which contains 60% (molecular) of NaCl, melts at  $450^{\circ}\text{C}$  [250]. However, sodium has a much stronger affinity for chlorine than does magnesium. Sodium reduces  $\text{MgCl}_2$  completely at temperatures above  $800^{\circ}\text{C}$ . Thus, if the  $\text{TiCl}_4$  is reduced with a mixture of sodium and magnesium, the magnesium may completely suppress the sodium as a reducing agent, so that the reduction produces NaCl practically

exclusively instead of a chloride mixture until all of the sodium has been used up. Thus, the first stage of the process must be run above 800°C, and only during the second stage, when all of the sodium has been used up and the magnesium has begun to react, does the melting point of the salt mixture begin a gradual decline. In addition to these difficulties, the presence of  $\text{MgCl}_2$  in the reaction mass endows it with the shortcomings of the magnesiothermic reaction mass and greatly complicates its refinement. All of the above tends to discourage the use of this method. Nevertheless, there have been a number of proposals for the use of the method for the design of equipment for continuous reduction (see Chapter 13).

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Heavy patenting of various improvements to the sodiothermic reduction of titanium has continued in recent years. Thus, in the USA and Great Britain alone, about 250 patents on this subject were awarded in 1964-1966. Most of these patents have been concerned with the production of higher-grade, coarse-grained metal by the two-stage process and the development of equipment for continuous reduction.

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- 333 <sup>1</sup>G.V. Chernov. Author's abstract of dissertation, Moscow, 1963.
- 338 <sup>2</sup>V.A. Shubin. Author's abstract of dissertation, Moscow, 1958.
- 340 <sup>3</sup>See also V.A. Shubin. Author's abstract of dissertation, Moscow, 1958.
- 341 <sup>4</sup>V.A. Shubin. Author's abstract of dissertation, Moscow, 1958.
- 354 <sup>5</sup>V.A. Shubin. Author's abstract of dissertation, Moscow, 1958.
- 359 <sup>6</sup>Patent (USA), No. 2,527,443, 1951.
- 361 <sup>7</sup>See also Patent (Australian), No. 221,279, 1958; Patent (USA), No. 3,022,158, 1962; 3,022,159, 1962; Patent (Japanese), No. 4656, 1956; Patent (British), No. 805,076, 1958.
- 363 <sup>8</sup>Patent (USA), No. 2,846,303, 1958.
- 363 <sup>9</sup>Patent (USA), No. 2,835,568, 1958.
- 364 <sup>10</sup>Patent (USA), No. 2,846,303, 1958.
- 364 <sup>11</sup>Author's certificate (USSR), No. 117,645, 1959.
- 364 <sup>12</sup>Patent (USA), No. 2,936,232, 1960; 3,022,158, 1962; No. 2,986,462, 1961; Patent (Japanese), No. 4656, 1956; Patent (British), No. 805,076, 1958.

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- 364 <sup>13</sup>Brochure of Imper. Chem. Ind. (ICI), Wrought Titanium, 1956.
- 366 <sup>14</sup>Patent (Belgian), No. 567,529, 1960; Patent (USA), No. 2,618,550, 1959; No. 2,618,549, 1959.
- 366 <sup>15</sup>Patent (British), No. 697,530, 1953.

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Symbol List

| Manu-<br>script<br>Page<br>No. | Russian | When<br>Typed | Meaning |
|--------------------------------|---------|---------------|---------|
| 331                            | пж      | п             | melting |
| 331                            | хип     | б             | boiling |

Chapter 16

THE HYDROMETALLURGICAL PROCESS FOR REFINEMENT  
OF THE REACTION MASS

Features of the Hydrometallurgical Process

The titanium can be separated from the reaction mass produced by reduction of  $TiCl_4$  with magnesium or sodium by either of two fundamentally different methods: driving the chloride and the excess of the metallic reducing agent out of the titanium at temperatures above  $800^\circ C$  in a vacuum or leaching the soluble components of the reaction mass out of it in dilute acid solutions.

The first of these methods was examined above. It has the following basic shortcomings:

a) the process is intermittent, relatively unproductive, complex, and expensive;

b) at a high temperature in a vacuum, titanium sinters into a dense block and welds to the reactor walls; this makes extraction and subsequent crushing difficult;

c) at high temperatures in a vacuum, it is difficult to prevent induction of air into the reactor and contamination of the titanium by oxygen and nitrogen; the titanium is also contaminated by iron, nickel, chromium, and other impurities when it interacts with the reactor material at high temperature;

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d) inclusion of the vacuum-separation process in the reaction-mass-purification flowchart is an obstacle to higher  $TiCl_4$  reduction rates, since fast delivery of  $TiCl_4$  into the reactor results in an extremely dense block of titanium sponge, and this greatly complicates distillation of the chlorides out of the deep layers of the block in vacuum separation and produces what is known as underseparated sponge.

The hydrometallurgical process does not have these drawbacks and is highly productive and continuous; the equipment required for it is much simpler.

However, this method also has major shortcomings:

a) metallic reducing agent is lost during leaching of the reaction mass;

b) oxidation of the titanium in its reaction with the solution and its contamination by oxides of the metallic reducing agents and by absorption of hydrogen formed in the reactions of the metallic reducers and lower titanium chlorides with the solution are detrimental to the quality of the titanium;

c) if a magnesiothermic reaction mass is being processed, some of the magnesium chloride is hydrolyzed during leaching and the hydrate residues, which cannot be completely eliminated from the titanium sponge by leaching, interact with the titanium during the remelting that follows, contaminating it with oxygen and hydrogen;

d) in the hydrometallurgical process, it is necessary to evaporate down large quantities of solutions containing magnesium or sodium chlorides and to dehydrate the salts obtained after evaporation. Dehydration of magnesium chloride is a complex, time-consuming, and expensive process.

As we know, the magnesiothermic reaction mass was processed hydrometallurgically early in the history of titanium technology. Later, because of the above shortcomings, hydrometallurgy was supplanted in a number of cases by vacuum separation, and the quality of the metal improved. Nevertheless, the hydrometallurgical process was used until recently to refine magnesiothermic

reaction mass at one of the largest titanium plants in the USA, the plant at Henderson [92].

Under industrial conditions, sodiothermic reaction mass is processed exclusively by the hydrometallurgical method. In this case, the quality of the metal has been higher than that of metal refined by vacuum separation.

In selecting the process for reaction-mass treatment, therefore, it is necessary to devote careful and discriminating analysis and evaluation to the advantages and disadvantages of the two methods, which depend on a number of factors.

The material composition of the reaction mass is the prime determining factor in the refining process. Table 34 gives guideline compositions for reaction masses produced by the magnesiothermic and sodiothermic methods [106, page 68; 298].

The chief difference between the magnesiothermic and sodiothermic reaction masses is that the former has a high content of magnesium that has not been utilized in the process and practically none of the lower titanium chlorides. In addition, the  $MgCl_2$  content of the reaction mass is much lower than the NaCl content in the latter case. This is because the NaCl is not drained during reduction in the sodiothermic process, while the  $MgCl_2$  is periodically tapped from the reactor in the magnesiothermic method.

TABLE 34  
Reaction Mass Compositions, % (by mass)

| Reaction mass   | Metallic titanium | Reducing metal (Mg, Na) | Lower titanium chlorides, converted to titanium | $MgCl_2$ or NaCl |
|-----------------|-------------------|-------------------------|---|------------------|
| Magnesiothermic | 50-70             | 30-35                   | None  | 15-20            |
| Sodiothermic    | 15-25             | 0.1-1.0                 | 0.1-3.0   | 75-85            |

A distinctive feature of the sodiothermic reaction mass is the practically total absence of unreacted sodium. The sodium

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residues, which amount to 0.1-1.0%, are for the most part dissolved in NaCl, although some sodium is occasionally present in the form of fine beads in the reaction zone. Another characteristic is the presence of lower titanium chlorides, which are usually dissolved in the NaCl and endow the reaction mass with various shades of color ranging from light green to violet and black.

Magnesium is practically insoluble in water, although it dissolves well in acidified water. The rate of solution depends on the surface area presented by the metal, the acidity of the solutions, the salt content in the reactor, and solution temperature. Large amounts of heat (110 kcal per gram-atom of magnesium) and hydrogen (about 2.0 liters per gram-atom of magnesium) are released as magnesium dissolves in an acidified solution. If the magnesium content in the reaction mass is high and the solution volume small, the solution is heated to boiling, which results in vigorous oxidation and hydrogenation of the titanium. To avoid reactor overheating, it is necessary to increase the liquid:solid ratio and cool the solution.

Sodium reacts violently with water and acidified solutions. This calls for precautionary measures in leaching out sodiothermic reaction mass. The reaction of sodium with water releases 57.6 kcal/g-atom of sodium, but only half the amount of hydrogen liberated on solution of magnesium. The solution is warmed by only a few degrees during leaching of sodiothermic reaction mass that does not contain free sodium, so that it is usually unnecessary to cool the solution.

During the leaching process, the lower titanium chlorides present in the reaction mass react with neutral and especially with alkaline solutions to form insoluble hydroxides and oxychlorides, which concentrate on the surface and in the pores of the metal and contaminate it with oxygen on subsequent remelting.

The lower titanium chlorides become soluble in acidified aqueous solution. Precipitation of the hydroxide residues out of acidified solutions takes a very long time. The rate of

precipitation increases rapidly with rising temperature [288].

To prevent hydrolysis of lower titanium chlorides and contamination of the metal by hydrolysis products during leaching of the reaction mass, solution acidity and temperature must be watched carefully during the process.

Lower titanium chlorides are often present in the reaction mass in complex-salt form. These salts react with the solution just like the individual lower chlorides, but the reaction is somewhat slower.

#### Behavior of Titanium Powder and Sponge in the Hydrometallurgical Refining Process

One of the most important factors determining the rate of the process and the reaction of the titanium with the solution, the oxides, and the gases during hydrometallurgical treatment of the reaction mass is the specific surface area of the powder or sponge.

Titanium powders and sponges are agglomerates of crystals ranging in size from fractions of a millimeter to several millimeters. The structure of the basic mass of crystals is dendritic. Crystal size depends on the nature of the reduction reactions, the reaction rate, temperature and pressure in the reactor, the distribution of the crystals in the reaction mass, and other factors that are difficult to take into account.

Vacuum-separated magnesiothermic sponge that was originally produced in a reactor from which the  $MgCl_2$  was tapped is much coarser and denser than sodiothermic powder produced by single-stage reduction and hydrometallurgical reaction-mass treatment.

Table 35 gives granulometric compositions and Table 36 specific surface areas for magnesiothermic sponge and sodiothermic powder [106, page 68; 229].

Specific areas were determined by B.V. Deryagin's method [290] for the fine fractions, and for the coarse fractions on the basis of measurements of the specific surfaces of fine fractions taken from the same consignment and comparison of the rates of solution of the fine and coarse fractions.

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TABLE 35  
Granulometric Compositions of Sponge and Powder

| Magnesiothermic sponge |      | Sodiothermic powder |      |
|------------------------|------|---------------------|------|
| 1                      | 2    | 1                   | 2    |
| -80 +12                | 78,0 | +2,4                | 6,0  |
| -11 +6                 | 12,0 | -2,4 +1,05          | 7,4  |
| -6 +3                  | 6    | -1,05 +1,17         | 10,1 |
| <2                     | 4    | -1,17 +0,83         | 15,3 |
|                        |      | -0,83 +0,80         | 8,4  |
|                        |      | -0,80 +0,42         | 12,2 |
|                        |      | -0,42 +0,39         | 11,1 |
|                        |      | -0,39 +0,21         | 9,0  |
|                        |      | -0,21 +0,15         | 8,2  |
|                        |      | -0,15 +0,10         | 5,6  |
|                        |      | -0,10 +0,07         | 3,1  |
|                        |      | <0,07               | 3,6  |

1-Fraction (mm)

2-Yield of fraction, %  
of total sample mass

TABLE 36  
Specific Surface Areas of Titanium Sponge and Powder

| Fraction,<br>mm | Specific surface, m <sup>2</sup> /g |                        |
|-----------------|-------------------------------------|------------------------|
|                 | Magnesiothermic<br>sponge           | Sodiothermic<br>powder |
| +2,5            | 0,33                                | 0,57                   |
| -2,5 +1,6       | 0,22                                | 0,57                   |
| -1,6 +1,0       | 0,51                                | 0,86                   |
| -1,0 +0,63      | 0,80                                | 0,74                   |
| -0,63 +0,40     | 0,77                                | 0,74                   |
| -0,40 +0,32     | 0,76                                | 0,70                   |
| -0,32 +0,25     | 0,80                                | 0,77                   |
| -0,25 +0,16     | 0,82                                | 0,83                   |
| -0,16 +0,10     | 0,90                                | 0,80                   |
| -0,10 +0,063    | 0,97                                | 0,94                   |
| -0,063 +0,06    | -                                   | 1,0                    |
| -0,06           | 1,13                                | 1,30                   |

As we see from Table 36, titanium sponge and powder have developed surfaces. Although the specific surface areas of like fractions of magnesiothermic sponge and sodiothermic powder differ only slightly, the specific surface area of the material as a whole is several times larger in the case of the sodiothermic

powder because the yield of fine fractions from that powder is several times the corresponding yield from magnesiothermic sponge. This explains the higher activity of this powder in reactions and adsorption.

It has been established by V.A. Aleksander and L.M. Pidzhen [291] that titanium is oxidized by atmospheric oxygen even at temperatures above 25°C. It has been reported that titanium reacts with water only at temperatures above 100°C [291]. L.V. Biryukova et al. [106, page 68] established that the oxygen content of the titanium is about 0.025% when the reaction mass is leached out at 30-40°C, but increases to 0.10% at 100°C, 0.15% at 150°C, and 0.20% at 200°C. Given the developed surface of the titanium sponge or powder, this increase in oxygen content strongly influences metal quality. For this reason, hydrometallurgical treatment of the reaction mass, and especially drying of the sponge, must be carried out quickly and at the lowest possible temperatures. It has also been found that the rate and degree of oxidation of titanium in air are practically the same as for oxidation in water.

Hydrogen is liberated during hydrometallurgical refinement of reaction masses containing magnesium, sodium, and lower titanium chlorides, and the titanium becomes saturated with it. The hydrogen is no great obstacle to the acquisition of high-grade titanium, since it is eliminated quite completely from the metal during subsequent high-temperature vacuum remelting. However, hydrogen saturation of the titanium complicates melting in vacuum arc furnaces by causing the metal to bump and spatter, with the result that the melting regime is unstable and large amounts of metal are lost. In some cases, it is necessary to remelt the titanium ingots a second time to eliminate all of the hydrogen from the titanium.

Hydrogen is released for the most part as a result of solution of metallic reducing agent that has not been utilized in the reduction process. As we noted above, there are particularly large amounts of unutilized reducer in magnesiothermic reaction mass. A small amount of hydrogen is released when  $TiCl_2$  reacts

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The hydrogen content in the metal depends on the contents of magnesium, sodium, and lower titanium chlorides in the reaction mass, the acid concentration in the solution, and the time and temperature of leaching and drying. Various inhibitors are used to protect the metal from hydrogen contamination; these are surfactants that coat the surface of the titanium with a thin film and protect it not only from hydrogenation, but also from oxidation and solution in the acid. Another protection method consists in binding the hydrogen into chemical compounds as soon as it is released. Use of  $\text{FeCl}_3$ ,  $\text{Cu}_2\text{Cl}$ ,  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{NaNO}_3$ , oxalates, potassium formate, chlorine,  $\text{MnO}_2$ , and  $\text{CuSO}_4$  is recommended for this purpose.  $\text{FeCl}_3$  and  $\text{Cu}_2\text{Cl}$  are used as inhibitors more frequently than the others [106, page 68; 245].

The hydrogen content in magnesiothermic sponge leached out without inhibitors runs to a few tenths of a percent, or several times as much as when inhibitors are used. The metal's hydrogen content is no more than 0.03-0.05% when sodiothermic reaction mass, which contains practically no metallic sodium, is leached out. Even in this case, however, it is advisable to use inhibitors if this makes it possible to produce titanium with lower oxygen and hydrogen contents and reduce the losses of titanium dissolved in the acid bath. On the other hand, in introducing an inhibitor, it is necessary to make certain that it does not contaminate the titanium sponge or powder.

It is known that, despite the high chemical stability of compact titanium, titanium sponge and powder are soluble to a certain extent even in dilute (0.5-1.0%) hydrochloric acid solutions because of their large specific surface areas. As a result, some loss of titanium with the solutions is inevitable in hydrometallurgical treatment of the reaction mass.

The highest rates of solution of the metal are observed when a freshly cleaned titanium surface interacts with an acid solution. However, if the cleaned titanium surface is exposed to air for a certain time, its rate of solution in the acid drops sharply, since an extremely thin film of acid-insoluble oxides forms on

the surface of the metal. Thus, despite the large specific surface areas of titanium sponge and powder, their room-temperature solubilities in 0.5-1.0% hydrochloric acid solutions are only about 0.5%.

Titanium sponge and powder can adsorb salts and oxides. This interferes with their complete elimination from the metal. As a rule, most of the salt is removed during the first 10-15 minutes of leaching, and then the rate of salt elimination from the metal declines. For example, the NaCl content in the powder may be down to 0.25-0.50% after leaching of a sodiothermic reaction mass in fresh solution, but removal of the salt then practically ceases.

The sizes of the leached particles, porosity, the sizes of the pores, and their arrangement and structure are of great importance for complete removal of dissolved impurities from titanium sponge and powder. Closed pores are formed during crystallization of the titanium and especially during mechanical crushing of the sponge. It is practically impossible to remove salts and metallic reducers in closed pores by leaching.

The most serious shortcoming of the hydrometallurgical method applied to reaction masses, especially those of sodiothermic origin, is oxygen contamination of the metal. Oxygen enters the titanium as a result of hydrolysis of lower titanium chlorides and as a result of the metal's reactions with water and acid during leaching and drying. As we noted above, leaching in 0.5-1.0% hydrochloric acid solution prevents the formation of hydroxides in the solution and contamination of the metal by these hydroxides. Here it must be remembered that the concentration of the acid in the solution must be high enough to prevent hydrolysis and precipitation of titanium hydroxide from the solution, but not so high as to dissolve the titanium rapidly. The solution must not be hot, since titanium hydroxide forms much more rapidly in hot than in cold solutions. To prevent hydrolysis of the lower titanium chlorides, the reaction mass must not be exposed to the open air, but should be treated with the acid solution as quickly as possible.

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The other source of oxygen contamination in titanium -- its reaction with water and atmospheric oxygen -- can also be controlled rather well. Here the basic problem is that of reducing the metal's reaction surface area. As we know, the finest particles present the largest surface areas. Taking advantage of the fact that fine-grained titanium is easily ground, the quality of most of the metal can be improved by screening the fine fractions out of it. This involves losses of the metal, but these are to a certain degree inevitable. Another approach is to conduct the reduction process under conditions that favor formation of coarse-grained titanium sponge and powder.

The effects of high temperature and process time during leaching and drying on the content of oxygen in the titanium can be minimized. For this purpose, leaching should be done in cold solutions, and the material should be dried quickly and at the lowest possible temperatures. The current drying formula is 1-2 hours at 100-110°C.

It has been established that with an average titanium-sponge specific surface area of 1000-2000 cm<sup>2</sup>/g [328] and a properly organized hydrometallurgical process, oxygen contamination of the sponge during leaching amounts to a few hundredths of a percent.

Use of nonaqueous solvents for leaching the reaction mass is attractive. One such solvent is methyl alcohol. However, NaCl has a very low solubility in this alcohol (0.15%), and this is an obstacle to its practical use. Attempts have been made to leach with liquid ammonia.<sup>(1)</sup> At 30°C, 19.7% Na and 4% NaCl dissolve in 100 parts (by mass) of ammonia. Since the solubility of NaCl is comparatively low, leaching requires a large amount of ammonia and several stages, which makes it uneconomical. In addition, sodium and the lower chlorides react with NH<sub>3</sub> at higher temperatures, forming ammonia-insoluble compounds. These compounds remain in the titanium powder and contaminate the metal with nitrogen when it is melted, to the great detriment of its mechanical properties.

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Footnote (1) is on page 392.

### Refinement of Magnesiothermic Reaction Mass

As we noted earlier, two fundamental difficulties are encountered in this refining method: the high content of unutilized magnesium in the reaction mass and the ability of the lower crystal hydrates of magnesium chloride to hydrolyze during dehydration to form MgO, which is insoluble in dilute hydrochloric acid solution and other acids.

The high magnesium content in the reaction mass results in the evolution of large amounts of heat and hydrogen during leaching. This results in losses and hydrogenation of titanium. In addition, solution of the magnesium involves substantial losses of metal and uses a large amount of acid. The high rate of acid consumption requires continuous replenishment of the leaching solution, since reduced acidity results in the formation of titanium hydroxide in the solution, and this, as we noted earlier, causes contamination of the titanium with oxygen and sharply lowers the quality of the metal.

In leaching magnesiothermic reaction mass, it is first necessary to take all measures to prevent overheating of the solution. It is not advisable to lower the temperature of the solution by increasing its volume, since this requires equipment with very large capacity and a large amount of process solution. Moreover, it is impossible to avoid local overheating at the reaction-mass-solution interface during leaching. Warming of the solution and local overheating can be prevented by lowering the leaching rate sharply with simultaneous cooling and vigorous agitation of the solution, but this entails a decrease in equipment productivity and makes the equipment more expensive. It is not now possible to prevent oxidation of the titanium by introducing inhibitors into the solution, simply because inhibitors of adequate effectiveness that do not contaminate the titanium are not available.

Leaching of magnesiothermic reaction mass involves the transfer of large amounts of magnesium chloride and magnesium into the solution. Subsequent evaporation of the brine and dehydration of the magnesium chloride in particular are very difficult and expensive processes.

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As we know, the crystal hydrates of magnesium chloride contain from one to 12 water molecules in different temperature ranges [292]. Thus, the crystal hydrate with 8 water molecules is stable up to  $-3.4^{\circ}\text{C}$ , the hydrate with 6 molecules up to  $117^{\circ}\text{C}$ , the hydrate with 4 molecules to  $182^{\circ}\text{C}$ , and the hydrate with 2 molecules of water up to  $240^{\circ}\text{C}$ . Thus, even at high temperatures magnesium chloride contains substantial amounts of water. To accelerate dehydration of these crystal hydrates, it is necessary to secure the largest possible difference between the equilibrium water-vapor pressure above the hydrate and the partial pressure of the vapor in the surrounding atmosphere. This can be done by heating the hydrate to a temperature near the critical point. Then, however, it must be remembered that magnesium chloride crystal hydrates are capable of melting incongruently in their own water of crystallization, followed by thickening, which makes dehydration extremely difficult. In practice, therefore, they are dehydrated at temperatures below the critical points.

Hydrated  $\text{MgCl}_2$  dehydrates without appreciable decomposition only when it contains 2 water molecules. At  $182^{\circ}\text{C}$ ,  $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$  begins to decompose hydrolytically, with evolution of hydrogen chloride.

In the  $304\text{--}554^{\circ}\text{C}$  range, the hydrate decomposes in accordance with the reaction



and at temperatures above  $554^{\circ}\text{C}$  by the reaction



To prevent hydrolysis, it is necessary that the ratio of the partial pressure of  $\text{HCl}$  to that of the water in the gaseous phase above the magnesium chloride crystal hydrate be larger than the equilibrium constant of the reaction at the particular temperature. For this purpose, dry hydrogen chloride, which must be synthesized in a special reactor, is fed into the drying unit. All of these measures greatly complicate the dehydration process and increase its cost.

In spite of all this, however, the hydrometallurgical process for leaching magnesiothermic reaction mass is sometimes used under industrial conditions owing to its high productivity, simplicity, reliability, and low equipment outlay [299, 301]. For example, the American firm TMCA leaches magnesiothermic reaction mass with a tubular leacher made of titanium; it is about 2.5 m in diameter and 20 m long [301].

TABLE 37  
Quality of Magnesiothermic Sponge Obtained After Vacuum Separation and Hydrometallurgical Processing of Reaction Mass

| Magnesiothermic sponge <sup>1</sup> | Designation | Chemical composition, % not above |       |      |      |      |       |      |      |
|-------------------------------------|-------------|-----------------------------------|-------|------|------|------|-------|------|------|
|                                     |             | N                                 | C     | Cl   | Fe   | Si   | Mn    | Mg   | Mg   |
| Leached                             | ML 120      | 0.02                              | 0.025 | 0.15 | 0.10 | 0.04 | 0.03  | 0.04 | 0.4  |
| Separated                           | MS 120      | 0.02                              | 0.025 | 0.12 | 0.15 | 0.04 | 0.005 | 0.05 | 0.05 |

<sup>1</sup>HB = 120.

Technologies for the hydrometallurgical processing of magnesiothermic reaction mass are still being developed. As the magnesiothermic reduction is improved, the degree of magnesium utilization in the reactor will increase and, consequently, its content in the reaction mass will be lowered. This may substantially simplify the hydrometallurgical process applied to the reaction mass and make it possible to produce high-grade titanium.

Substantial interest attaches to industrial-scale experiments with the so-called combined method of reaction-mass processing.

As we know, the greater part of the magnesium chloride and practically all of the magnesium are distilled out of the reaction mass during the first few hours of the process in vacuum separation. It takes about 70% of the separation time to reduce the magnesium chloride content from 2-5 to 0.02-0.12%. Thus, on completion of the first stage of vacuum separation, the reactor can be cooled and the reaction mass extracted from it at a 2-5% MgCl<sub>2</sub> content and subjected to hydrometallurgical treatment. At

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this point, the reaction mass contains practically no metallic magnesium, and its magnesium chloride content does not exceed 2-15%. Thus, the losses of metal can be cut sharply, evolution of hydrogen in the leaching process can be reduced, and the magnesium chloride content in the solution, which must be evaporated down and dehydrated afterward, can be lowered. This reaction mass can be leached in 1% hydrochloric acid solution at a solid:liquid ratio of 1:10, a process that warms the solution by only a few degrees. Experiments in this direction are continuing.

As a basis for quality comparisons between magnesiothermic titanium produced by vacuum separation and metal produced hydro-metallurgically, Table 37 presents American technical specifications for these two types of titanium sponge [293].

Our attention is drawn to the higher contents of chlorine, hydrogen, and magnesium in sponge produced by leaching the reaction mass, and its lower iron content. This is consistent with the causes and sources of titanium contamination in the hydrometallurgical process and the peculiarities of the process as we have examined them. Unfortunately, comparable data on the oxygen contents in types ML120 and MS120 titanium are not available.

#### Processing of Sodiothermic Reaction Mass

On the basis of the aspects of the hydrometallurgical process that we discussed above, and with consideration of the chemical composition of sodiothermic reaction mass, the following technology may be used to process it.

On extraction from the retort, the reaction mass is quickly treated with dilute acid solution to prevent hydrolysis of the lower titanium chlorides. It is then crushed to 3-10 mm. Leaching is carried out in an open-type apparatus with protective louvers and efficient exhausting of the gases released. Leaching is usually a two-stage process. During the first stage, a 1% solution of hydrochloric acid is used at a solid:liquid ratio of 1:4 for quick and complete binding of the metallic sodium, while the second stage uses a 0.5% solution at the same solid:liquid ratio. It is preferable to work with S:L = 1:10, but this

requires evaporating down a large amount of solution, and this is uneconomical. The solution is agitated during leaching and the temperature in the tank is held at the 20-30°C level. The first leaching takes from 30 minutes to 1 hour, and the second from 1 to 2 hours. After leaching, the powder is thoroughly washed with distilled water to rinse out as much of the salts as possible. The powder can be dried in a vacuum or in a current of hot air at 100-110°C.

Let us examine the technology used by the firm Electrometallurgical (Ashtabula plant, USA) for reaction-mass processing [245, 244].

The reactor is opened after cooling to the ambient temperature. Precautionary measures must be observed here, since there is a possibility of deflagration of sodium and finely dispersed titanium that have settled on the walls, shield, and cover of the reactor.

Then the reactor, which is 75-80% filled with reaction mass, consisting of 17% Ti and 83% NaCl, is set up on a turntable for extraction of the reaction mass. The mass is removed from the reactor by cutting it out on a machine fitted with a special milling cutter in an air atmosphere (see Fig. 45).

As we noted earlier, sodiothermic reduction produces titanium in the form of fine particles distributed through a large volume of sodium chloride. For this reason, the titanium powder that forms is not as tough as magnesiothermic sponge, welds to the retort walls, and can therefore be removed from the reactor comparatively easily by machine cutting of the reaction mass. Since the titanium is dispersed through a large volume of sodium chloride, the probability and degree of its oxidation in the cutting process do not present the same hazard as in the magnesiothermic process, and no special measures are required to prevent oxidation of the titanium powder during this operation.

After cutting out, the reaction mass is loaded into special two-ton-capacity sealed bins, which are mounted on dollies. Before leaching, the reaction mass is passed through a magnetic

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separator to remove metal chips that may have entered it while the reaction mass was being cut out, as a result of accidental milling of metal from the reactor walls.

After magnetic separation, the reaction mass is passed through a sifter with holes 10 mm in diameter. After sifting, the fraction finer than 10 mm is loaded into a reactor for leaching, and the fraction larger than 10 mm is crushed on a hammer mill, separated magnetically, sifted, and then sent for leaching.

Graphic Not Reproducible



Figure 63. Reaction-mass leacher.

The reaction mass is leached in 6 reactors about 3 meters in diameter and 3.5 meters high, with rubberized walls and agitators (Fig. 63). A single reactor load of reaction mass weighs 2 tons. The material is loaded with a certain amount of caution, since sodium-bead inclusions are encountered in the reaction mass, as are lower titanium chlorides. The hydrogen evolved as the sodium reacts with the solution is suctioned continuously out of the

reactor. Leaching takes about 30 minutes in a 0.5-1% hydrochloric acid solution. Then, to separate the solution, the pulp from the reactor is loaded into a centrifuge 1.5 meters in diameter, which turns at 500 rev/min (Fig. 64). A synthetic fabric is used as the filtering material in the centrifuge. Centrifuging takes about 20 minutes and is followed by thorough washing of the titanium powder with distilled or filtered water right in the centrifuge.

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Figure 64. Centrifuge.

From the centrifuge, the washed titanium powder is sent for drying in a horizontal vacuum-drying furnace 3 meters long and 1.5 meters in diameter. Drying is carried out at 80-100°C and a residual pressure of 50 mm Hg with agitation, which is effected with a hollow shaft fitted with rakes. During drying of the powder, which takes 2 hours, steam is fed into the agitator shaft and the drier jacket; when drying is complete, water is sent through to cool the titanium powder. Before unloading, the drier is filled with an inert gas to protect the powder from oxidation

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1% hydrochloric pulp from the diameter, which is used as the takes about the titanium centrifuge.

during the removal operation. The dried powder is thoroughly stirred to average its composition and then made up into consignments weighing up to 6 tons. The section in which the operations of screening, stirring, and packaging of the titanium powder are carried out is provided with strong ventilation and dust traps.

The centrifuged sodium chloride solution is returned to a nearby sodium plant, where it is evaporated down, dried, and sent for electrolysis. The same solution is discarded at the British Wilton plant [296].

In principle, sodiothermic reaction mass can be vacuum-separated in the same way as magnesiothermic material, since the vapor pressures of sodium chloride and metallic sodium are quite high at 950-1000°C. However, the hydrometallurgical treatment is simpler, more productive, and cheaper. Moreover, the titanium sinters into a solid block during vacuum separation, and it is difficult to remove it from the reactor.

#### Structure and Quality of Sodiothermic Powder

The titanium powder produced by sodiothermic reduction differs greatly in structure and particle size from titanium sponge produced by the magnesiothermic method.

TABLE 38  
Mechanical Properties of Sodiothermic Titanium

| Grade of titanium | Hardness, HB | Ultimate strength, kgf/mm <sup>2</sup> | Terminal elongation, %, not below |
|-------------------|--------------|--|-----------------------------------|
| 120               | 120          | Not above 42                           | 20                                |
| 130               | 130          | 35-36                                  | 15                                |
| 150               | 150          | About 49                               | 15                                |
| 160               | 160          | 50                                     | 12                                |

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Unlike magnesiothermic sponge, which comes in a large spongy mass, sodiothermic powder has grain sizes ranging from 1.6 to 0.12 mm, and the particles of sodiothermic titanium are acicular.

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Table 35 gives the granulometric compositions of sodiothermic powders produced by Electrometallurgical at Ashtabula, USA.

Table 32 listed American technical specifications as to the mechanical properties and chemical composition of titanium produced by various methods.<sup>(2)</sup> As we see from this table, the permissible chlorine content in sodiothermic titanium of the highest grade is 2.5 times that for the magnesiothermic product. As we explained above, this is because the chlorine is for the most part bound here into NaCl, which, unlike MgCl<sub>2</sub>, does not hydrolyze during dehydration. The higher chlorine content in sodiothermic titanium does not appear to complicate remelting in vacuum-arc furnaces to any appreciable degree. A rather high hydrogen content, 0.0125%, is permitted in sodiothermic titanium, while only 0.005% is accepted in separated magnesiothermic sponge. The permissible iron content in sodiothermic titanium is 25% lower than that in the magnesiothermic metal. When the latter is produced by leaching reaction mass, the permissible-hydrogen content is almost 2.5 times that for the sodiothermic metal. This is because of the intensive hydrogenation of the titanium during leaching of reaction mass that contains large quantities of magnesium that has not reacted in the reduction process.

The sodiothermic titanium actually produced by the Electrometallurgical firm contains 0.01-0.15% O<sub>2</sub>, 0.01-0.7% C, 0.001-0.02% N<sub>2</sub>, 0.005-0.019% H<sub>2</sub>, and the better specimens have hardnesses from 110 to 130 HB [300].

Table 38 gives the requirements of the British standard for leached sodiothermic titanium [245].

The average hardness of British sodiothermic powder is 110 HB.<sup>(3)</sup> It has been reported that sodiothermic titanium with better plasticity than the magnesiothermic metal can be produced under industrial conditions [245].

It has been established that if sodiothermic powder is smelted in a hard vacuum (about 60 μm), the amount of oxygen in the ingot does not change from its content in the powder, while the amount of hydrogen is reduced to 0.003%; in a relatively soft

Footnotes (2) and (3) are on page 392.

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vacuum (300-400  $\mu$ m), ingot oxygen content rose to 0.15%, while  
the hydrogen content remained practically unchanged. Smelting  
of sodiothermic powder differs from smelting of magnesiothermic  
sponge in that it evolves much larger amounts of gas, and this  
complicates the process, requiring provision of a more powerful  
vacuum system and additional precautionary measures.

Footnotes

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- 381 <sup>1</sup>Patent (West German), No. 1,029,166, 1961
- 390 <sup>2</sup>Book ASTM Stand., 1958, Vol. 7, 741
- 390 <sup>3</sup>Brochure of Imper. Chem. Ind., Wrought Titanium, 1956;  
Patent (British), No. 776,739, 1957.

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## Chapter 17

### CONTINUOUS TITANIUM PRODUCTION PROCESSES

#### General Information

1956; The existing batchwise processes for the reduction of titanium and purification of the reaction mass cannot be regarded as rational for large-scale titanium production, since these conditions make it difficult to build large industrial plants equipped with small numbers of highly productive units and capable of producing the metal cheaply enough.

The basic source of the difficulties encountered in designing a continuous titanium production process is the fact that the reaction in which titanium tetrachloride is reduced by magnesium or sodium produces titanium particles that sinter together at elevated temperatures to form titanium sponge, which adheres tightly to the walls of the reactor (or shell insert) and is therefore impossible to remove from the apparatus without interrupting the technological process.

To devise a continuous titanium production process, it will be necessary to provide for charging the reactor with the starting materials and removal of the reduction products from it without stopping the process or at least without opening up the apparatus.

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A continuous reduction process should give a substantial equipment-productivity increase over the existing batchwise processes. The reduction products should also be refined to titanium in continuous or highly productive intermittent equipment.

The titanium particles formed in the continuous process should be quite coarse to ensure high quality in the metal; it will otherwise be necessary to devote one of the stages to enlargement of the metal particles.

On the basis of technical-economy considerations, it will probably be expedient to use one of two metallic reducing agents in a continuous metallothermic process: sodium or magnesium.

A comparative evaluation of the two reducers indicates that from the standpoint of use in the design of a continuous reduction process, each of them has its advantages and disadvantages.

Thus, the advantages of sodium are its low melting point (98°C), which makes it easier to pipe and deliver to the reactor in liquid form; its inertia with respect to the structural materials with which it comes into contact, and plain and stainless steels in particular; the rapidity of the reduction reaction; the high (practically 100%) utilization of sodium in the process; insignificant adhesion of the reaction mass to the reactor wall; the possibility of extracting the titanium from the reduction products by leaching, i.e., by a comparatively simple, cheap, and highly productive operation.

A deficiency of sodium as a continuous-process reducing agent is that it has a high vapor pressure at the temperatures used in the process, and this promotes the development of undesirable gaseous-phase reduction reactions. Moreover, the reaction in which titanium tetrachloride is reduced by sodium is accompanied by a large heat effect, which may make it difficult to withdraw the excess heat and, consequently, lower process productivity [307].

Magnesium has a number of disadvantages when compared with sodium from the standpoint of continuous reduction process design: a higher melting point (651°C), reactions with stainless steel,

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and a density in the liquid state that approaches that of magnesium chloride, so that they are difficult to separate into layers. However, magnesium also has attractive properties: a relatively low vapor pressure at the reduction temperatures and a substantially smaller reaction heat effect.

Thus, both magnesium and sodium are of practical interest for the elaboration of a continuous process. The many variants that have been proposed for continuous metallothermic titanium production indicate that it is being worked on in earnest. Since it is not yet clear which of the many possible avenues will be taken by the development of the continuous metallothermic process, it will be in order to discuss the proposed principals, including some that may not appear promising at the present time.

Much attention will be devoted to the patent literature along with published papers on the problem, which are few in number. The material will be organized by processes instead of by metallic reducing agents, since the patents usually cite all or almost all of the alkali and alkaline-earth metals as reducing agents.

#### Early Work on Continuous-Process Development

The early — relatively speaking — papers devoted to finding a continuous metallothermic method for titanium production have two distinctive features. Out of inexperience and lack of awareness of the difficulties that would arise, attempts were made to arrive at a continuous process by carrying out all of the production stages in a single complicated unit: reduction of the titanium from  $TiCl_4$ , separation of the titanium from the excess reducing agent and chloride, and even smelting of the titanium ingots. A second feature of these proposals was their ignorance of various aspects of the process that would preclude practical workability, primarily underrating of the ability of titanium to weld to the inner surface of the apparatus.

One version of an installation for continuous production of titanium, which was proposed in 1950, and combines all of the above processes [302], appears in Fig. 65.

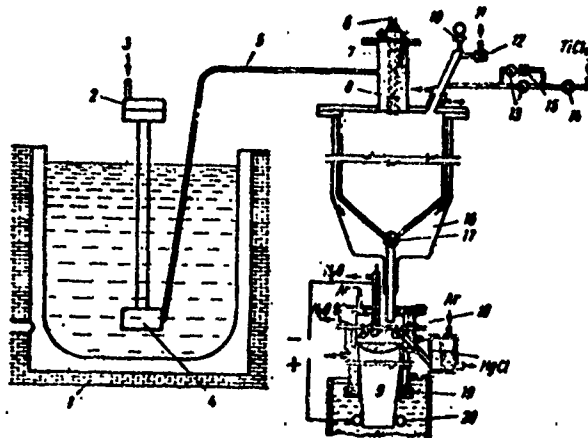


Figure 65. General form of experimental apparatus for continuous production of titanium ingots from titanium tetrachloride and magnesium. 1) Furnace for melting magnesium; 2) pump compressed-air motor; 3) air; 4) centrifugal pump; 5) heated pipeline; 6) valves for magnesium; 7) electrical level regulator; 8) magnesium (760°C); 9) titanium ingot; 10)  $TiCl_4$  pressure gauge; 11) to exhaust stack; 12) safety valve for  $TiCl_4$ , operated off pressure gauge; 13) needle valves; 14) pump for  $TiCl_4$ ; 15)  $TiCl_4$  delivery controller, operated off pressure gauge; 16) salt bath; 17) cock; 18) water-cooled tungsten electrode; 19) packing; 20) contact and extractor rolls.

The reduction unit consists of two basic parts: a device for constant-rate (0.23-0.67 kg/min) delivery of molten magnesium and a device for injection of liquid titanium tetrachloride. The  $TiCl_4$  flowrate is automatically controlled to keep its vapor pressure in the 50-160-mm Hg range. Reduction is carried out in an inert-gas (argon) atmosphere. To prevent the formation of lower titanium chlorides, the temperature is held in the 730-870°C range throughout the reaction chamber by a circulating salt bath that simultaneously cools hot areas and warms cool ones.

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In attempting to put the laboratory installation to work, its authors came up against considerable experimental difficulty, which made it impossible to keep the entire unit or even its individual components working smoothly for any length of time. The apparatus did not work long enough at a time to answer the question as to whether obstruction of the holes for admission of the reactants or welding of the titanium to the walls of the reaction chamber could be eliminated during regular operation.

With the object of overcoming the difficulties associated with transport of the reduction products from the reduction chamber to the arc furnace, another proposal for continuous titanium production equipment<sup>(1)</sup> calls for a different method of extracting the reduction products from the reactor. In this method, the sponge is extracted from the base of the reactor with one or another type of mechanical appliance and transferred, still hot (at a temperature above the melting point of magnesium chloride) and without exposure to air to a bin from which the still uncooled sponge is delivered into an arc furnace for melting.

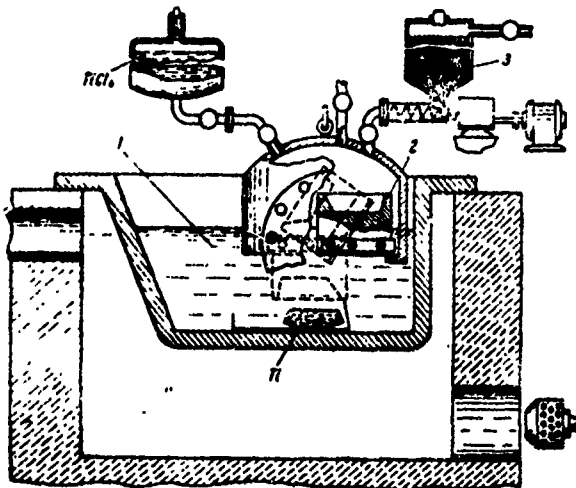


Figure 66. Diagram of apparatus for production of titanium in a fused salt bath. 1) Bath; 2) graphite crucible; 3) metallic magnesium particles.

Footnote (1) is on page 445.

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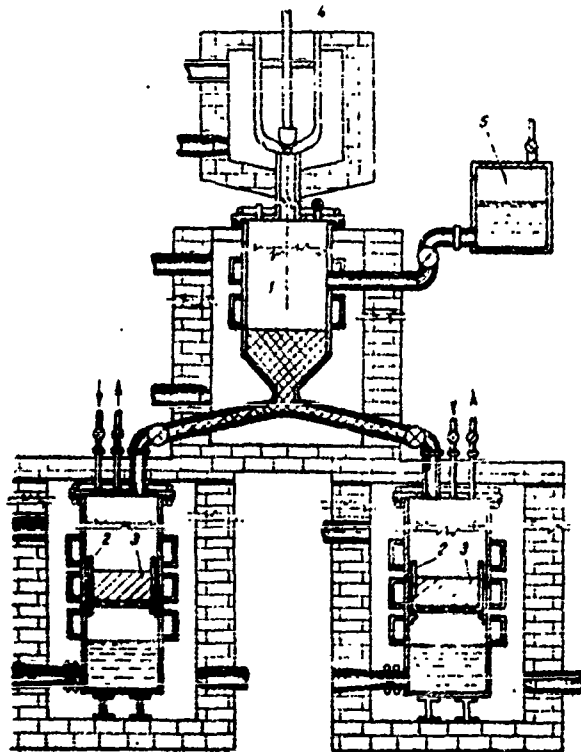


Figure 67. Diagram of installation for continuous titanium production.

According to a patent description,<sup>(2)</sup> titanium tetrachloride is reduced by magnesium in an inert-gas atmosphere in a graphite crucible under a bell the bottom of which is immersed into a fused salt bath (Fig. 66). When the crucible is full of titanium sponge, it is dumped; the sponge is to drop to the bottom of the bath, from which it can be extracted without stopping the process.

According to another patent,<sup>(3)</sup> the process is to be carried out in an ordinary reactor, which is connected to two receivers to facilitate continuous operation (Fig. 67). It is proposed that the titanium particles, which are heavier than magnesium chloride, will drop to the floor of reactor 1. The reaction products are drained as necessary into alternating receivers 2, which

Footnotes (2) and (3) are on page 445.

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hold pots 3 with perforated bottoms. The titanium particles are caught here, while the magnesium chloride drains to the chamber floor. Magnesium is supplied to the reactor from smelter 4, and the titanium chloride from tank 5.

Although it could easily be established, even at the time at which the proposals were made, that such combination units were unworkable, patents for similar machinery continued to appear for some time.

Subsequently, however, much more attention was devoted to methods for separate accomplishment of the reduction and removal of the reaction mass. Attempts were made to eliminate adhesion of titanium particles to the walls of the apparatus. In one proposal, for example,<sup>(4)</sup> the reducing agent was to be melted in a salt bath, and an impeller was used to set up circulation from the periphery toward the center in order to prevent contact between the reducing agent and the reactor walls (Fig. 68).

#### The Jet-Droplet Process

To prevent contact between the molten reducing agent and the walls of the reaction equipment and welding of titanium particles to these walls, it was proposed that liquid reducing metal be admitted to the reactor in the form of individual droplets or a jet that would break up into droplets during its flight. The reducer was to be introduced along the central axis of the unit to prevent its coming into contact with the reactor walls. To prevent welding of the reaction products to the equipment, they were also to be kept out of contact with the walls until they had been cooled to temperatures at which this welding no longer occurs.

Footnote (4) is on page 445.

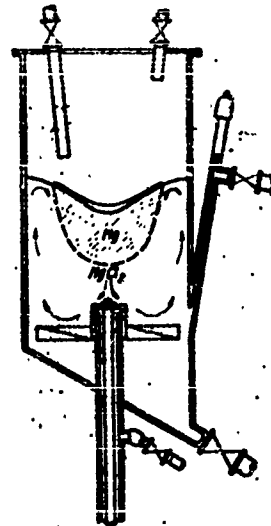


Figure 68. Diagram of reduction apparatus designed to eliminate adhesion of titanium to reactor wall.

One of the patents<sup>(5)</sup> proposes that molten reducing agent be pressed through a perforated plate into a reactor placed beneath it and taking the form of a long vertical tube. The tube diameter was to be chosen so as to exclude contact between the reduction products and its walls. The reaction tube was filled with titanium tetrachloride vapor, and its pressure was held in a range that would ensure an excess of the tetrachloride over the reducing agent.

The reduction reaction takes place during the descent of the metallic reducer droplets through the tube and the titanium tetrachloride vapor. Here, according to the authors of the patent, the reducing agent is completely consumed, and the reaction products have time to solidify and cool adequately by the time they reach the collector at the bottom of the reaction tube. This makes it impossible for them to agglomerate and stick to the receiver walls.

Since the descent of the droplets takes very little time, no more than 1-2 seconds, provision must be made for the highest possible rate of the reduction reaction. For this reason, the authors recommend a magnesium-calcium alloy rather than magnesium as the reducing agent. It is reported that less than half the time is required for reduction of titanium tetrachloride when the magnesium contains 5% calcium than when it is the only reducing agent. It is more advantageous to use an alloy containing 82% Mg and 18% Ca, which melts at 516°C.

The powdered products — magnesium chloride, calcium chloride, and titanium — that are formed by the reduction reaction are to be separated mechanically and then leached out.

Another patent<sup>(6)</sup> takes account of the short fall time of the reducing-agent droplets and proposes that it be made possible for the reducing metal to react with liquid  $TiCl_4$  rather than with its vapor, i.e., for a substantially longer span of time.

The principle of this method is as follows. The liquid metallic reducer is admitted in the form of individual droplets or a continuous stream at the top of a sealed steel unit containing the

Footnotes (5) and (6) are on page #45.

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liquid  $TiCl_4$  reducing metal generated from a mixture of reducing metal and reducer and by tangential contact with a stirrer. The rate of contact between the metal and the surface.

The effect of the walls of the reactor from which the titanium is reduced.

Reduced metal which, on descending to the bottom of the reactor, is further processed.

The amount of titanium chloride check indicates the reduction rate but also a sponge impurity on the surface of the titanium chloride granule.

Since the reaction rate is low, it is necessary to include a filter into the system.

In the magnesium Footnote

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liquid  $TiCl_4$ . After striking the  $TiCl_4$  bath, the droplets of reducing metal float on its surface in an envelope of vigorously generated  $TiCl_4$  vapor. To prevent contact between the droplets of reducing agent and the new reaction products, and between the reducer and the reactor walls, the  $TiCl_4$  bath is set in rotation by tangential delivery of the  $TiCl_4$  into the reactor or by use of a stirrer. A concave meniscus whose configuration is determined by the rate of agitation is formed as the bath turns. It prevents contact between the droplets of reducer and the reactor inner surface.

The exothermic heat of the reaction is dissipated by cooling the walls of the equipment with water and evaporation of part of the titanium tetrachloride. The vapor is diverted to a condenser from which the liquid titanium tetrachloride is returned to the reactor.

Reduction results in formation of reaction-mass granules, which, on cooling in the bath of boiling titanium tetrachloride, descend to the floor of the apparatus and are taken from it for further processing.

The authors of the patent make no mention of the lower titanium chlorides that are inevitably formed in this process. A check indicated that this is a very important point, since the reduction proceeds not only in an excess of titanium tetrachloride, but also at comparatively low temperature. The shell of titanium sponge impregnated with magnesium chloride that forms on the surface of the droplet makes it difficult for the titanium tetrachloride to react further with the magnesium enclosed within the granule.

Since, in addition to the titanium and magnesium chloride, a reaction-mass granule produced in a "droplet" unit must also contain lower titanium chlorides, it would be absolutely necessary to include further reduction of these lower chlorides to the metal into the process flowchart.

In a patent<sup>(7)</sup> awarded 10 years later, it is proposed that the magnesium be introduced in the form of -0.06-mm powder into Footnote (7) is on page 445.

a reactor filled with  $TiCl_4$  vapor in order to eliminate this shortcoming. The top of the reactor is heated to 450-550°C, which is enough to initiate the reduction reaction. The reaction is complete, even with such fine magnesium particles, only at the bottom of the reactor, on the surface of the boiling titanium tetrachloride. The envelope of titanium tetrachloride vapor that forms around the reacting magnesium particle not only carries it into the reaction zone, but also insulates it thermally, preventing it from cooling and thus sustaining the reduction process. The patent description says nothing to indicate whether these innovations prevent the formation of lower titanium chlorides, and does not indicate which methods the authors of the patent would propose for subsequent processing of the reaction mass.

#### Mobile Bed Reduction

Proposals for conduct of the reduction reaction in a mobile bed of solid reducing-metal chloride; e.g., in a "fluidized bed," have the object of permitting reduction of  $TiCl_4$  at low temperature, thereby excluding cohesion of the titanium particles into a single block, eliminating welding of the metal to the walls of the equipment, and simultaneously preventing the formation of a crust of reducer chloride, which blocks access of one reactant to the other. Since magnesium is not active enough at comparatively low temperatures and its use can result only in formation of lower titanium chlorides, sodium is recommended as the reducing agent when the mobile bed principle is used.<sup>(8)</sup>

A fluidized bed of sodium chloride particles is formed in the reactor by blowing a mixture of argon and  $TiCl_4$  [5-10% (by volume)] into it at the bottom.

The sodium is introduced at the top of the reactor in a small excess over the stoichiometric amount in order to prevent formation of the lower chlorides.

The process temperature range is 480-620°C. These temperatures are high enough to obtain a fast reaction and prevent formation of lower titanium chlorides. At higher temperatures, the sodium chloride begins to lump and the process breaks down. To

Footnote (8) is on page 445.

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prevent local hot spots, coolers filled with oil or, even better, liquid sodium or an Na-K alloy are placed inside the reactor.

Since a substantial excess of sodium in the fluidized bed favors coalescence of the NaCl particles with the newly formed titanium, the sodium content in this bed should represent no more than 1% of its mass.

The titanium particles settle on the grains of salt. As the reaction advances, the fluidized bed becomes deeper, and part of it is removed from the reactor at intervals and sent for further processing. The sodium is fed into the reactor after heating to 150°C at a rate of 44 g/hour per cm<sup>2</sup> of fluidized-bed cross section. It is recommended that the velocity of the vapor-gas mixture delivered to the reactor be held at around 0.15 m/s.

Since the titanium is produced in a highly dispersed form, methods have been proposed for increasing particle size. It has been proposed that the reaction products be held above the melting point of NaCl for several hours for this purpose;<sup>(9)</sup> provision is also made for agitating the solid reaction products for 5-7 hours at 700-750°C.<sup>(10)</sup>

To improve the process in which the reduction products are refined, it has been proposed that the mixture of solid sodium chloride and titanium particles be withdrawn at the top of the reactor by a horizontal worm and transferred into a basket in a retort at a temperature above 800°C.<sup>(11)</sup> When filled, the basket is raised to the top of the retort, some of the sodium chloride is drained from it, and the titanium content in the melt rises from 17 to ~50%, thus accelerating aggregation during subsequent high-temperature holding. This holding becomes unnecessary if the titanium remaining after drainage of the salt is pressed at a temperature above 800°C. The titanium content in the resulting blocks can be brought up to 95%. It is proposed that this material be sent directly for remelting.

In one of the more recent patents,<sup>(12)</sup> it is correctly observed that holding the reaction products for many hours to aggregate the titanium particles cancels the advantages of continuous titanium production.

Footnotes (9), (10), (11) and (12) are on page 445.

To eliminate this deficiency, this patent proposes that the reaction products be fed from the reduction apparatus into a slightly inclined pipe and pressed down through it by a piston at 850-950°C at a rate such that the titanium remains in the pipe for about 1 hour. The excess of the metallic reducing agent and its chloride are drained from the pipe through holes made in it and at its lower end. If sodium is used as the reducer, much of it will be evaporated from the pipe. Compacting results in a compact block of reaction products containing 30-40% Ti. Before further processing, this block can be cut up or crushed.

Processes in which titanium chloride is reduced in a "fluidized bed" have other shortcomings in addition to the above: the need for precise observance of temperature conditions, since a temperature decrease slows the process and results in formation of lower titanium chlorides, while an increase in temperature above the acceptable limit causes lumping of the salt and makes it necessary to stop the process to clean the reactor. The narrow temperature range of the process may also limit reactor productivity by making it necessary to remove large amounts of heat from it. Since the process may be run at comparatively low temperatures — below the melting point of the reducing-metal chloride, it appears that only sodium can be used as a reducer in this process.

Undesirable links in the technological process include the operation of holding the reaction products for many hours at high temperatures to enlarge the titanium grains (although there is, as we noted above, a way to eliminate this operation) and the need to remove dusty and perhaps pyrophoric reaction products from the argon before recycling it.

Nevertheless, the highly efficient application of the "fluidized bed" process elsewhere in the chemical industry indicates that it should not be rejected without adequate experimental testing.

Together with use of the "fluidized bed," many of the patents describe mechanical agitation of the sodium and sodium chloride. For example, it has been proposed that  $TiCl_4$  be reduced

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by sodium in the 150-350°C range in a horizontal reactor fitted with a longitudinal bladed shaft. (13)

To avoid coalescence of the reaction products, considerable quantities of recycled products are fed into the reduction apparatus in order to hold the sodium content at or below 3% in the material into which the titanium tetrachloride is fed.

Mixers, (14) conveyors, (15) and worms (16) have also been suggested as agitating devices. The patents also note the need to have a sodium chloride excess and therefore call for returning large amounts of the products into the reactor [up to 20 parts (by mass) per 1 part sent for further refining]. The titanium particles are first aggregated by holding the material for several hours at a temperature above the melting point of sodium chloride, i.e., at 850-950°C.

One reduction process is designed to eliminate the operation of aggregating the titanium particles. (17) A mixture of solid sodium chloride and titanium powder with grain sizes no larger than 1.25 mm is fed into a reactor fitted with an agitating device rotating at 50 rev/min. Then a mixture of fused lower titanium chlorides with NaCl and liquid sodium are fed into the reactor in the stoichiometric quantities. The reduction takes place in an inert-gas atmosphere at 500-600°C.

The amount of reactants taken should represent about 25% of the mass of the materials present in the reactor. Some of the reaction products are removed from the reactor and screened. The coarse fraction is leached in a solution of some mineral acid, while the fine fraction is returned to the reactor. The grain size of the material sent for leaching is regulated by varying the stay time of the reactants in the reducing apparatus, screening through a coarser screen, and increasing the percentage of material returned to the process. It is reported that this method can produce titanium powder in grain sizes of 0.63-0.16 mm.

Another patent (18) describes an improvement of the process examined above. (19) The dispersed product obtained in a low-temperature reduction is loaded onto a platform conveyor that passes

Footnotes (13), (14), (15), (16), (17), (18) and (19) are on page 445.

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through a furnace at 850-900°C. About 75% of the molten sodium chloride included in the reaction mass drains off the conveyor into a collector. The conveyor carries the titanium granules to a disintegrator for crushing. They are then leached out in 1% HCl solution.

In a variation of this process, the dispersed reaction products are pressed before loading into the conveyor furnace. It is reported<sup>(20)</sup> that briquettes 36 mm in diameter and 20-50 mm high can be produced under a specific molding pressure of 270-300 kgf/cm<sup>2</sup>. The conditions under which the briquettes are processed in the conveyor furnace are the same as those for the loose mass.

#### Reduction in Injector-Nozzle Equipment

In developmental work toward continuous metallothermic titanium production, a certain amount of attention has been devoted to the use of nozzles to vaporize the reactants. It was felt that atomizing the reactants would make it possible to produce titanium in dispersed form, eliminate welding of the titanium to the reactor walls and formation of the reaction-product "bridge," and result in smaller excesses of reducing metal. One patent<sup>(21)</sup> proposes that the "jets" of dispersed sodium and TiCl<sub>4</sub> vapor be aimed at angles such that they impinge on one another at the middle of the reactor. It is assumed that the temperature in the reaction zone will exceed the boiling point of the sodium chloride, whose vapor will escape into a condenser, while the titanium powder settles to the floor of the reactor.

According to the patent claims, which are confirmed by theoretical calculations and experiments as they apply to the sodiothermic reduction [303], the vapor of the metallic reducing agent reacts quite vigorously with the TiCl<sub>4</sub> vapor, forming a flame in which the temperature reaches 2000°C, i.e., exceeds the melting point of titanium. For this reason, several of the proposals for injector processes envisage the use of reaction heat not only to vaporize the reactants and the chloride of the reducing metal as it forms, but also simultaneously for melting the

Footnotes (20) and (21) are on page 445 and 446.

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One of the early reports on the laboratory-scale development of a continuous titanium production process [304, 153] describes a unit in which magnesium vapor formed by utilizing the heat of the reduction reaction is entrained by a current of argon and introduced into the reaction zone, where it reacts with the  $TiCl_4$  vapor. The dispersed titanium particles that are formed are trapped in cyclones set up in series with the reactor. On emerging from the reactor, the argon stream is divided into two parts: 90% of the Ar is sent for mixing with magnesium vapor and recycling, and 10% to the cyclones to settle the magnesium dust. According to one report [153], the reaction products contained no lower chlorides or titanium tetrachloride at all and had the approximate composition 19.5% Ti, 77.5%  $MgCl_2$ , and 3% Mg, which corresponds to a 15% magnesium excess.

It has been established that the grain size of the titanium powder depends on the rate of the reduction reaction. This gave rise to the hope that a comparatively large-grained product could be obtained. However, experiments failed to produce titanium of satisfactory quality. The lack of a simple and inexpensive method of processing dispersed titanium into compact metal was apparently the reason for suspending developmental work on this process.

In one patented process,<sup>(22)</sup> an arc into which a magnesium wire is fed burns between two electrodes in an injector leading to the reactor. The wire melts and is atomized by blowing titanium tetrachloride through the injector. The powder produced by the reaction settles to the conical floor of the reactor, from which it is raked into a vertical worm installed in the center of the reactor floor for extraction from the reactor. The temperature in the reactor is held in the 760-870°C range.

Later proposals call for certain equipment refinements. For example, one patent<sup>(23)</sup> describes a cylindrical reactor 1 (Fig. 69) whose reaction space 2 is surrounded by an annular chamber 3, which is packed with titanium fragments (4). The  $TiCl_4$  vapor is fed through pipe 5 into an ejector device 6 of the Venturi type with a flared stack. The molten magnesium moves through pipe 7

Footnotes (22) and (23) are on page 446.

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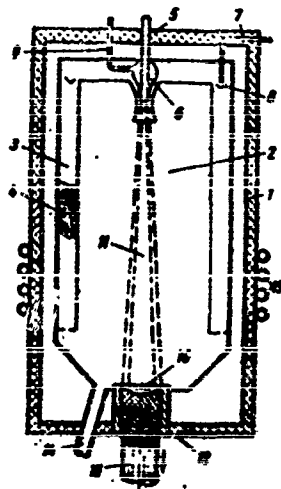


Figure 69. Diagram of apparatus for production of titanium by continuous injector-nozzle process.

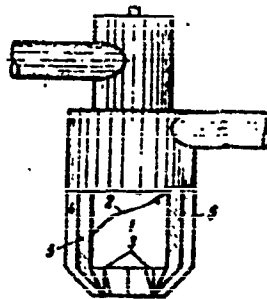


Figure 70. Diagram of obstructionproof injector nozzle.

into an annular distribution trough 8, from which it spills into the titanium packing and is vaporized from it by the reaction heat. The resulting magnesium vapor is drawn into ejector 6. Argon is fed into ejector 6 through pipe 9. To permit use of sodium in addition to magnesium as the reducing agent, the design includes a pipe through which sodium vapor passes into the annular gap around the  $TiCl_4$  delivery pipe 5. The incandescent torch 11 of reaction products is aimed at the surface of the liquid titanium 10 in crystallizer 12, which is situated at the bottom of the reactor and has cooled walls. As the titanium accumulates in the crystallizer, the ingot 13 that is formed is extracted from it at the bottom. The magnesium chloride vapor condenses outside the torch, on the inner surface of chamber 3, and the liquid salt drains to the reactor floor and is removed from it through pipe 14. Some of the titanium mixes with the chloride and is withdrawn from the reactor with it. The titanium is separated from this salt by filtration or some other method. Coil 15 is filled with the liquid metallic reducing agent and serves to cool the reactor

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The development of a cooling system for the vapor. The density and the titanium dioxide reaction chamber vapor going to 1000°C, of the

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during operation and warm it up before starting the process. In another patent,<sup>(24)</sup> which provides for the use of sodium as the reducing agent, the reactor is to be placed in a liquid-sodium bath to withdraw the excess heat, and the top of the reactor is to be cooled by circulating fused sodium chloride. To prevent the reaction products from building up on the injector, there are two concentric annular gaps in the nozzle around the central  $TiCl_4$  delivery orifice; sodium vapor is fed into the outer gap and argon into the inner one to prevent the sodium vapor and  $TiCl_4$  from interacting in the immediate vicinity of the injector.

The proposals in another patent<sup>(25)</sup> represent a further development of the patents examined above.<sup>(26)</sup> For example, a remote cooling system is provided to condense most of the sodium chloride vapor. The walls of the reaction chamber are made from molybdenum and heated to about 1400°C. Some of the NaCl vapor condenses on the walls of the reaction chamber, washing away the titanium deposits on these walls. The liquid sodium around the reaction chamber is heated to the boiling point, with some of the vapor going to a reflux condenser and some of it, after heating to 1000°C, to the injector. The crystallizer for continuous casting of the titanium ingot is also sodium-cooled.

A unit of this type is also proposed in another patent,<sup>(27)</sup> which provides for introduction of a consumable titanium electrode containing alloying additives into the reactor.

Some patents describe other features designed to eliminate buildup of reaction products on the injector. They note that even partial obstruction of the injector passages by reaction products may change the direction of the torch or the proportions of the initial reactants in it, thus disturbing the process. The injector must therefore remain perfectly clean during operation. One patent<sup>(28)</sup> proposes that the metallic reducer be introduced through the central injector orifice and the  $TiCl_4$  vapor directly into the reactor. Fused salt is fed into an annular gap around the central injector tube, forming a protective liquid curtain around the jet of metal. The patent description states a typical reservation: for the proposed equipment to function properly, the Footnotes (24), (25), (26), (27) and (28) are on page 446.

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jet of metal must not, under any circumstances, be interrupted or allowed to shrink in diameter.

One patent<sup>(29)</sup> proposes that sodium vapor be introduced into the injector external annular gap 4 (Fig. 70). A mixture of  $TiCl_4$  vapor and droplets is introduced through the central pipe 1, which has spiral ribs 2. Centrifugal force presses the  $TiCl_4$  droplets against the inner surface of tube 1, forming a film of liquid  $TiCl_4$  on it. The ribs 3 slow the rotation of this film and force it to flow from the injector, forming a cylindrical liquid curtain that prevents reactions between the  $TiCl_4$  and Na vapors directly at the injector surface. Thus, the reaction zone is moved away from the injector. To prevent vaporization of the  $TiCl_4$  film from the inner surface of pipe 1 by the heat of the metallic-reducer vapor moving through annular space 4, a spacer 5 made from a heat-insulating refractory material is placed between the  $TiCl_4$  and sodium delivery pipes.

Another patent<sup>(30)</sup> devotes most of its attention to the reactor rather than the principle of the injector: the middle of the reactor is expanded considerably and vibrators are secured to the conical bottom of the reactor to prevent the reaction products from settling on the walls of the reduction apparatus.

Patent<sup>(31)</sup> describes an injector assembly (Fig. 71) consisting of a vertical tube 1 fitted with cooling jacket 2. Nozzle 3 with bore 4 for delivery of liquid or gaseous titanium tetrachloride and bore 5 for introduction of the liquid or gaseous reducing metal — sodium is recommended — is placed in the top of tube 1. The lower end of the injector is fitted with diffuser 6 and deflector 7, which direct the stream of tetrachloride against the walls of the reactor. Chamber 8 with water jacket 9 communicates with the reactor at its base. An inert gas is fed into chamber 8 through pipe 10. The reduction reaction takes place in the injector flame. Sponge titanium forms a liner 11, whose thickness increases downward as far as level 12, on the walls of the reactor. Below level 13, where reduction proceeds more rapidly, the sponge metal begins to melt and drain downward, forming a compact pipe 14, over whose inner surface liquid magnesium chloride drains

Footnotes (29), (30) and (31) are on page 446.

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The proposal assumes that the titanium pipe 14 formed on the liner layer can be extracted continuously from the reaction zone as a result of cooling the walls of reactor 1.

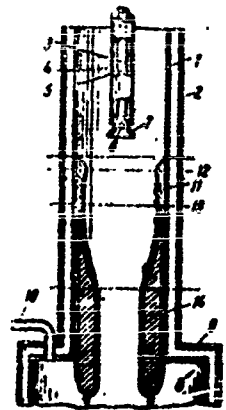


Figure 71. Diagram of apparatus for production of titanium by continuous injector process.

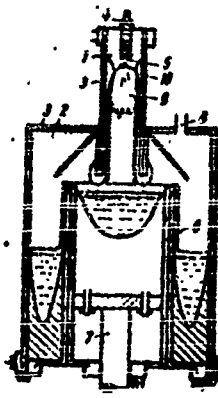


Figure 72. Diagram of apparatus for production of titanium by continuous injector process. 1) Reaction chamber; 2) reaction product collector; 3) cooling jacket; 4) injector nozzle; 5) spray nozzle; 6) crystallizer for titanium; 7) bottom-plate rod; 8) pipe connection for inert gas delivery; 9) reaction zone; 10) titanium liner.

Patents (32, 33) call for a somewhat different apparatus (Fig. 72). A crystallizer into which the reaction products — titanium and magnesium chloride — are drained is mounted below the reaction zone. Because of their considerable density difference, they separate into layers, the titanium freezes and is transformed into an ingot that can be extracted at the bottom, and the magnesium chloride overflows across the upper lip of the crystallizer, collecting in the outer annular space. Provision is made for extracting not only a titanium ingot, but also a titanium-and-salt block with a titanium core surrounded by frozen magnesium chloride.

Footnotes (32) and (33) are on page 446.

The authors of proposals calling for the extraction of liquid titanium as the direct product of the reduction reaction fail to take two fundamental points into account. Firstly, heat calculations indicate that to obtain the titanium in liquid form, it is necessary to introduce the reducing metal as a superheated vapor rather than a liquid, or, as some of the patents recognize, to provide supplementary heating of the reaction space.

It was confirmed experimentally in [324] that formation of solid lower titanium chlorides ceases at 850-900°C. However, the secondary reaction



starts to advance rapidly at temperatures in excess of 1000°C. Thermodynamic calculations for the reactions in which  $\text{TiCl}_2(\text{T})$  and  $\text{TiCl}_2(\text{gas})$  have confirmed that the free energy of the reaction forming  $\text{TiCl}_2(\text{gas})$  decreases with rising temperature and equals zero at 1467°C (1740°K) under standard conditions ( $p_{\text{TiCl}_2} = 1 \text{ atm}$ ).

If the vapor partial pressure  $p_{\text{TiCl}_2} = p_{\text{TiCl}_4} = 10^{-2} \text{ atm}$ , then  $\Delta Z = 0$  at 1237°C (1510°K), and when  $p_{\text{TiCl}_2} = p_{\text{TiCl}_4} = 10^{-3} \text{ atm}$ ,  $\Delta Z = 0$  even at 1087°C (1360°K). This casts doubt on the possibility of obtaining liquid titanium directly in the reduction apparatus, i.e., in an environment of gaseous titanium tetrachloride, unless measures are taken to suppress the above reaction leading to formation of gaseous titanium dichloride.

Other difficulties must also be overcome before the injector-nozzle version of the continuous process become workable. Since the solid titanium is produced in a finely dispersed form in an injector-type reactor, some of it will obviously be carried away with the reducing-metal salt. Separation of titanium from this salt is a complex and expensive operation involving substantial losses of the metal. It is also necessary to ensure trouble-free performance of the injector by making it impossible for titanium to settle on the surfaces of its parts. It has not yet been possible to keep the injectors working for any appreciable length of time in tests of injector processes (in spite of the large numbers of experiments that have been conducted).

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Nonetheless, the possibility of sustained injector operation in reactors for reduction of titanium tetrachloride with a solid titanium product is apparently not to be ruled out. The results of a Japanese study of the production of high-purity titanium by an injector process were published in 1961 [320]. The reactor was supplied through concentric injectors with titanium tetrachloride vapor (outer injector) and magnesium vapor (inner injector). The authors made no mention of injector buildups or measures taken to eliminate this phenomenon, although the tests ran for several hours. The process was conducted at a residual reactor pressure of  $10^{-3}$ - $10^{-4}$  mm Hg. The titanium settled on titanium shavings with which the reactor was packed and did not weld to the reactor walls. This formed a basis for the development of a semicontinuous process, for which a patent has been issued.<sup>(34)</sup> The reactor is enclosed in a chamber whose elevator bottom can be pressed against the reactor to form a tight seal.

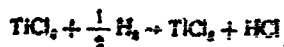
A pot filled with titanium chips is placed on this elevator base. When the titanium that has settled on the chips has filled the pot, it is lowered by elevator to a table at the bottom of the chamber and turned through 180°. Another pot of titanium chips has previously been set up on the other side of the table. When the table turns, the new pot moves into the reactor and the used one is withdrawn through an unloading hatch.

#### Reduction by Sodium in Two Stages

As we noted in Chapter 11, reducing titanium tetrachloride in two stages sets up conditions favorable for development of technology and equipment for semicontinuous and continuous processes. The conditions for reduction of the titanium tetrachloride by sodium are particularly favorable, since the lower titanium chlorides that form during the first stage of the process dissolve readily in the sodium chloride that also forms. During the second stage, the lower titanium chlorides, which have dissolved in the salt, can be completely and rather quickly reduced under conditions such that the titanium that is formed is isolated from the reactor walls and therefore will not weld to them.

<sup>(34)</sup>Footnote (34) is on page 446.

There have been a number of proposals for the use of hydrogen as an agent that reduces titanium tetrachloride to the lower chlorides. The thermodynamic characteristics of the reaction



and the disproportionation reactions that accompany it are given in Fig. 73.<sup>(35)</sup> Since the solubility of lower titanium chlorides in the NaCl melt favors the reduction of  $\text{TiCl}_4$  by hydrogen and increases the yield of lower chlorides, it is recommended that a mixture of  $\text{TiCl}_4$  and  $\text{H}_2$  be bubbled through an NaCl melt at a temperature around 900°C for the reduction reaction.<sup>(36)</sup>

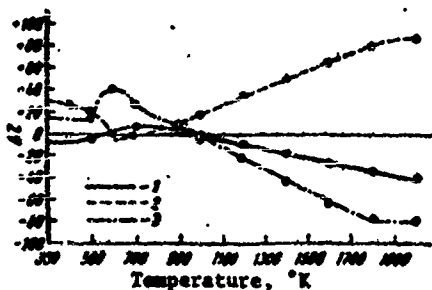
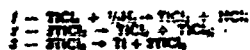


Figure 73. Thermodynamic characteristics of reduction of  $\text{TiCl}_4$  by hydrogen and the accompanying disproportionation reactions, kcal:



tium chlorides in it. For example, good results were obtained when a bath of fused NaCl or KCl was used. It has been reported, for example, that when a mixture of  $\text{TiCl}_4$  and  $\text{H}_2$  was fed backwards into a column through which fused NaCl was passed in the mass ratio  $\text{NaCl}:\text{TiCl}_4 = 3:1$ , and a  $\text{TiCl}_4$  delivery rate of 60 g/hour per  $\text{cm}^3$  of column cross section, about 97% of the  $\text{TiCl}_4$  was utilized. The process temperature was 850°C. The melt leaving the column contained about 26%  $\text{TiCl}_3$ .

Footnotes (35), (36) and (37) are on page 446.

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A number of ways of producing titanium continuously from its lower chlorides have been proposed.

Some of the patents take advantage of the property of lower titanium chlorides to disproportionate into chlorides of higher valency and titanium. This explains the interest shown in this titanium-production method: in principle, it opened the possibility of eliminating use of the reducing metal in the second stage of the process.

For example, one continuous method proposed for titanium production [310] is based on the fact that lower chlorides or bromides of titanium, especially the dihalides, can be produced by reacting the corresponding tetrahalide in vapor form with an initial material containing titanium dioxide mixed with carbon. The result of the reaction is a gas mixture containing the lower titanium halides and carbon monoxide. The lower halides disproportionate on heating in the gas stream under reduced pressure, yielding pure titanium and its higher halides.

S.I. Sklyarenko and S.F. Belov [311] showed that disproportionation of the lower chlorides is an extremely slow process, and hence hardly of practical interest as a variant of the continuous method. If ways were found to accelerate the disproportionation reactions significantly, the situation might be drastically changed.

Patent <sup>(38)</sup> describes one highly productive two-stage sodiothermic process. It is proposed that lower titanium chlorides be produced by reducing  $TiCl_4$  with sodium at  $790^\circ C$  with agitation. Enough sodium is introduced to support formation of the compound  $TiCl_2 \cdot TiCl_3 \cdot 3NaCl$  (26.5%  $TiCl_2$ , 34.5%  $TiCl_3$ , 39%  $NaCl$ ). The melt is cooled, and tablets weighing about 200 g are pressed from the resulting salt at  $100^\circ C$ . These tablets are introduced into a second-stage reactor filled with sodium at  $825^\circ C$  to complete the reduction. Reduction is complete within 3 minutes. The titanium granules that are formed retain the form of the tablets and can be removed from the reactor in this state for subsequent refining.

Footnote (38) is on page 446.

Patent<sup>(39)</sup> describes the second stage of a continuous process for production of coarse-grained titanium. Fused lower titanium chlorides are poured into crucibles and small amounts of sodium are placed on their surface. A "bridge" of titanium sponge is formed and ensures slow access of subsequent portions of the sodium to the fused lower chlorides. Toward the end of the crystal-growing process, the "bridge" is punctured at several points with a special rake. The crucibles with the melt are conveyed into a tunnel furnace heated to about 900°C and equipped with airlocks at its entrance and exit.

Processes for the production of titanium in combined apparatus have been patented for application to two-stage reduction. One such unit combines the functions of reducing the lower titanium chlorides to the metal, separating the metal from the chloride, melting the metal, and putting it out in the form of granules.<sup>(40)</sup> A solid charge consisting of lower titanium chlorides and dispersed solid magnesium is fed into the reactor by a worm in its floor. The reduction-reaction zone is provided with a jacket filled with fused salt. Circulation of the salt keeps the reaction-zone temperature about 50° above the melting point of the magnesium chloride, the excess of which leaves through holes in the sides of the reactor. As it forms, the titanium sponge is pushed up by the worm feeding the charge up into the burning zone of an arc in which the residual magnesium chloride is vaporized along with the excess reducer. The vapors of these substances are picked up by a current of argon forced into the reactor at the top, and carried by it into the reaction zone. The molten titanium overflows across the lip of the melting bath, and the balls formed as it freezes roll into a receiver set up beside the reactor.

Aluminum has also been proposed as a reducing metal for the two-stage process.<sup>(41)</sup>

The  $TiCl_4$  is reduced to the lower chlorides by aluminum powder with grain sizes smaller than 0.06 mm at 400-600°C. A mixture of  $TiCl_2$  and  $TiCl_3$  remains in the reactor, and the aluminum chloride is volatilized.

Footnotes (39), (40) and (41) are on page 446.

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The following equations

and

The lower titanium chlorides with aluminum and an inert gas are reduced in the briquet

Flush

It is found that titanium alloys

One process for the production of titanium is carried out in a tubular reactor. The air tube is filled with titanium chloride and the two stages of reduction and melting process

Among the various two-stage processes of the reduction

The reaction of the sodium chloride is fed into the reactor and passes through the surface of the  $TiCl_4$  excess and fusing down through the

Two methods are proposed for the reduction of  $TiCl_4$ .

Footnotes  
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The first stage of the process can be represented by the equations



and



The lower chlorides obtained in this way are crushed, mixed with aluminum powder, briquetted, and heated slowly to 1100°C in an inert atmosphere. The resulting titanium retains the shape of the briquettes.

Flushing with inert gas helps remove the  $\text{AlCl}_3$  vapor.

It is noted in the patent that formation of aluminum-titanium alloys is excluded in the two-stage reduction.

One proposal calls for combining the "fluidized bed" reduction process with the two-stage process.<sup>(42)</sup> The reduction is carried out in air tubes using argon as the pusher gas. In one of the air tubes, sodium is atomized on particles of NaCl and lower titanium chlorides produced by reduction of  $\text{TiCl}_4$  with sodium; the two streams converge in a third air tube, where the lower chlorides are reduced to the metal at a temperature below the melting point of NaCl.

Among the proposals concerning equipment for use in the continuous two-stage process, reactor designs in which both stages of the reduction are accommodated deserve special attention.

The reactor (Fig. 74) described in patent<sup>(43)</sup> is designed for the sodiothermic process and filled with sodium chloride; sodium is fed into the bottom of the reactor through pipe 1.  $\text{TiCl}_4$  vapor passes through pipe 2 and fills the gas space 3. Floating to the surface of the fused sodium chloride, the sodium reacts with the  $\text{TiCl}_4$  excess, forming  $\text{TiCl}_3$ , which dissolves in the melt. Diffusing downward, the  $\text{TiCl}_3$  reacts with the sodium droplets rising through the melt to form the titanium particles 8.

Two methods are provided for withdrawal of the excess heat from the reactor. The reactor cover 4 functions as a condenser for  $\text{TiCl}_4$ , droplets of which drain onto the surface of the NaCl

Footnotes (42) and (43) are on page 446.  
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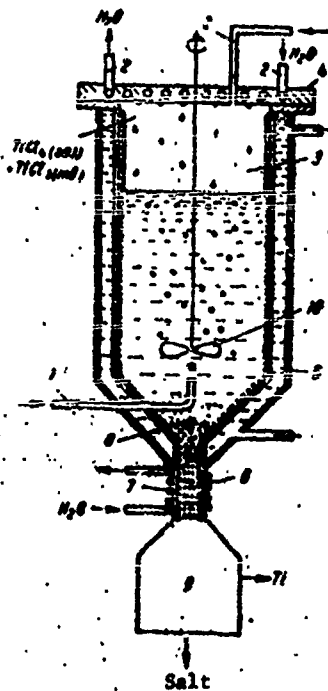


Figure 74. Diagram of apparatus for continuous sodiothermic titanium production.

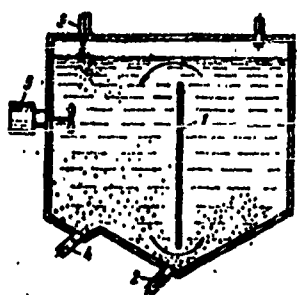


Figure 75. Diagram of apparatus for continuous titanium production by the magnesiothermic process.

melt and reevaporate, taking a certain amount of heat out of the melt. Heat is also taken off the reactor walls by fused sodium circulating in the cooling jacket 5. Agitator 10 in the reactor circulates the melt vigorously, thus preventing titanium particles smaller than 0.3 mm from settling to the floor. This requires circulation at a rate of around 10 cm/s. With time, the fine titanium particles aggregate and accumulate in the bottom of the reactor. Circulating the melt also improves distribution of the sodium in it and prevents the formation of a sodium chloride crust on the melt surface in spite of the rapid offtake of heat by the vaporizing  $TiCl_4$ .

To step up the formation of lower titanium chlorides in the top of the reaction, it is recommended that part of the  $TiCl_4$  be introduced through a bubbler placed just below the surface of the melt. It is assumed that the  $TiCl_4$  will react with titanium particles suspended in the melt, forming its lower chlorides.

The reactor has a conical bottom with a solid-salt plug 6. This plug is defrosted by shutting off the supply of water to coil 7 at periodic intervals for drainage of the titanium that has settled to the reactor floor together with the salt, from which it is separated, for example, on filter 9.

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Another reactor design that provides for the use of magnesium appears in Fig. 75.<sup>(44)</sup> Partition 1 separates the reactor into two sections. Titanium tetrachloride enters at the bottom of the right-hand section through pipe 2, which circulates the melt counterclockwise. Entraining fine titanium particles suspended in the melt, the  $TiCl_4$  reacts with them, forming the lower chlorides.

Magnesium enters at the top of the left-hand division through pipe 3 in the form of droplets or chips. The magnesium reduces the lower chlorides to the metal. Large titanium particles settle into pocket 4, while the fine ones are carried by the stream of melt into the right-hand division, where they react with the  $TiCl_4$ . A mechanical mixer 5 in the left-hand division of the reactor has the function of stepping up circulation of the melt.

It is recommended that the magnesium be introduced in the form of solid particles or droplets ranging in size from 0.15 to 6 mm. The titanium particles have sizes from 0.15 to 10 mm. It is assumed that the process can be run with the stoichiometric amount of magnesium.

#### Reduction by Bubbling Reactants Through the Melt

Researchers working on the development of a continuous titanium production process have returned repeatedly to the suggestion that the starting reactants be delivered into a fused salt bath covered by a layer of the molten reducing metal. These proposals have been based on the following premises: conditions under which the reduction will be complete within the melt of salts and reducing metal can be created inside the reactor; consequently, the initial reactants will be absent from the gas space of the apparatus, thus excluding formation of reduction products in this space. The reaction in the melt will produce dispersed titanium that will not stick to the walls of the reduction apparatus, but settle to the reactor floor, from which it can be extracted for subsequent refining.

According to one of the early patents,<sup>(45)</sup> this process would be carried out in a column filled with magnesium chloride, into

Footnotes (44) and (45) are on page 447.

which magnesium and  $TiCl_4$  would be delivered in vapor form. To complete the reduction of the lower titanium chlorides that are formed, it is proposed that the magnesium be introduced at a lower level than the  $TiCl_4$ . The reactants could also be delivered in liquid form. In this case, the rapid vaporization of the  $TiCl_4$  would help disperse the titanium product. The layer of melt in the column would have to be deep enough to give the reduction reaction time to go to completion.

The results of a study of conditions for continuous sodio-thermic titanium production by the bubbling method have been published [252].

The experiments were carried out in a reactor 75 mm in diameter and 400 mm high. To lower the process temperature, a eutectic mixture — 45%  $LiCl$  and 55%  $KCl$ , which melts at  $360^\circ C$  — was used as the salt bath. A bed of sodium 50-75 mm thick covered the melt. The  $TiCl_4$  vapor was introduced into the salt bed at a depth of 100-125 mm. The  $TiCl_4$  delivery rate was about 5 g/h per square centimeter of reactor cross section. The temperature range of the experiments was  $400-800^\circ C$ .

It was established that, regardless of the temperature and  $TiCl_4$  delivery rate, the reaction mass, which consisted of titanium, sodium chloride, and sodium, tended to collect at the top of the reactor in the form of an annular layer that clung to the reactor wall and the  $TiCl_4$  delivery pipe. A small part of the titanium formed lumps in the salt bed. In all experiments, only a small amount of titanium settled to the floor in the form of a fine black powder. This powder contained a substantial amount of oxygen and was apparently formed in the initial stage of the experiment by reaction of the first portions of reduced titanium with oxygen that was present, for example, in the sodium and the chloride.

In experiments run at temperatures below  $430^\circ C$ , some of the  $TiCl_4$  passed through the layer of melt into the reactor's gas space, and at higher temperatures all of the  $TiCl_4$  was reduced.

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Titanium built up on the  $TiCl_4$  delivery pipe in all experiments, especially when agitation of the melt was stepped up.

In some experiments, only sodium was delivered into the melt. The  $TiCl_4$  was fed into the reactor gas space at a pressure somewhat above 1 atm. This technique did not give any appreciable improvement.

The titanium dendrites that were found on the reactor floor in a number of experiments were apparently formed on interaction of dissolved reagents or reagents dispersed through the melt. Special experiments in which the starting materials were separated by fused salt were conducted to clarify this question. For this purpose, a pipe opening 100 mm below melt level was introduced into the reactor and the sodium was fed through it. The reactor's gas space outside the pipe was filled with  $TiCl_4$  vapor. Under these conditions, the reduction rate, which was determined by the rate of diffusion of sodium in the melt, was very low — about 1 g/h per square centimeter (counting the melt surface area in the  $TiCl_4$ -filled space). At the same time, only part of the titanium settled to the reactor floor. The rest of the metal settled on the reactor walls at the surface of the melt in the  $TiCl_4$  space.

In attempts to increase the rate of the reaction, the melt was agitated vigorously, and its level was lowered. However, the reaction rate could not be increased.

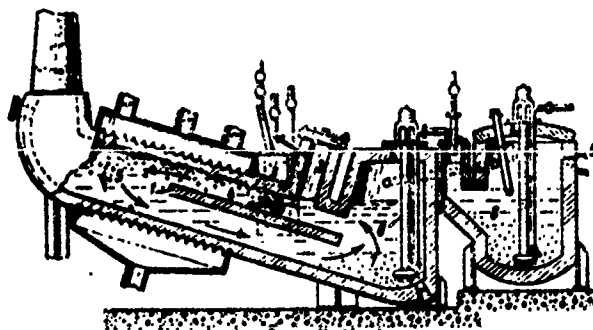


Figure 76. Diagram of apparatus for continuous titanium production by bubbling method.

Even though the experiments described above did not give the desired results, the data obtained give an idea of the difficulties that will have to be overcome for further development of the bubbling method: it will be necessary to keep the metallic reducing agent from entering the  $TiCl_4$  delivery feeder and to find ways to remove the reaction products from the inner surface of the reactor walls. It is claimed that the reduction reactions above the surface of the melt can be eliminated by introducing one of the reactants into the melt.

It appears that additional difficulties will arise when magnesium is used as a reducing agent because of the small difference between the densities of molten magnesium and magnesium chloride [313], which amount to about  $0.1 \text{ g/cm}^3$  at  $800^\circ\text{C}$ . When sodium is used as the reducing agent, the difference is about  $1 \text{ g/cm}^3$ , which favors accomplishment of the process by the bubbling method.

One proposal<sup>(46)</sup> calls for bubbling through an inclined reactor (Fig. 76) placed at an angle of  $\sim 30^\circ$  to the horizontal. Partition 1 is placed parallel to the longitudinal axis of the reactor to cause circulation of melt.  $TiCl_4$  vapor mixed with argon is fed through side chamber 2, in which the pressure is slightly higher than in the reactor. The molten magnesium enters through chamber 3. As they rise, the magnesium and  $TiCl_4$  react under the roof of space 4. There is always a layer of molten magnesium 5 on the melt surface in the reactor to prevent the  $TiCl_4$  from bursting out into the reactor's gas space. The titanium that is formed is carried away by the melt current into settling reservoir 7, from which pump 6 removes it from the reactor to settling tank 8. The excess magnesium chloride is released from the settling tank through spout 9.

The features of this unit include directional circulation of the melt, concentration of the magnesium and  $TiCl_4$  vapor under the roof of zone 4, and their slow ascent to the surface of the melt, which should help complete the reduction reaction. To prevent the new titanium from reacting with the surface of the roof in zone 4, it is recommended that this surface be faced with

Footnote (46) is on page 447.

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carbon plates, which could not but contaminate the titanium with carbon. Later, a patent<sup>(47)</sup> was awarded for a reactor filled with magnesium chloride under a layer of magnesium. A ring vault was immersed in the magnesium. An annular bubbling manifold for the titanium tetrachloride was placed on the floor of the reactor, and the tetrachloride reacted with the magnesium on the inner surface of the ring vault. The titanium deposited here was removed by a disk scraper. It dropped to the bottom of the reactor, from which it was extracted through the magnesium layer for subsequent refining.

Since introduction of the reactants into the reactor by bubbling produces dispersed titanium, it was suggested that they be compacted by pressing, which would, at the same time, permit continuous removal of the reaction products from the reduction apparatus.

According to one of the proposals,<sup>(48)</sup> the reactor working on this principle (Fig. 77) takes the form of a pipe 1 provided with an external gas heater 2. Titanium tetrachloride vapor from vaporizer 3 enters the retractable bubbler 4, which extends into chloride melt 5. A layer 6 of liquid magnesium covers this salt layer. Fresh magnesium — solid or liquid — is introduced into the reactor through pipe 7, and the excess magnesium chloride is removed through drainage unit 8. Reduction is carried out at a temperature of about 850°C in the reaction zone. On accumulation of a certain amount of dispersed titanium in the reactor, bubbler 4 is withdrawn from the reactor and hydraulic cylinder 9 is actuated to lower piston 10, which compacts the titanium in the bottom of the reactor, transforming it to a block 11 that contains about 90%

Footnotes (47) and (48) are on page 447.

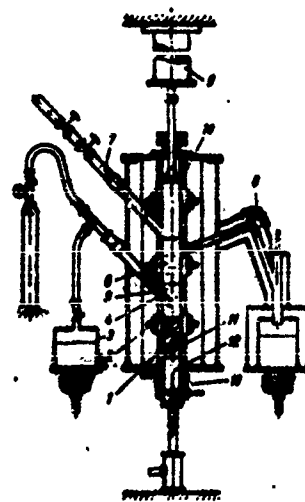


Figure 77. Diagram of apparatus for continuous titanium production with reaction products pressed out.

Ti (the remainder is magnesium and magnesium chloride).

During the initial phase of work with the reactor, formation of block 11 is assisted by back pressure created by the lower piston 12. As the height of block 11 increases, piston 12 moves down together with block 11; then they both leave the reactor through cooled crystallizer 13. Subsequent pressing of block 11 proceeds without piston 12, by friction of the block against the wall of reactor 1 and possibly of crystallizer 13.

The pressure applied to the block of titanium must be sufficient to compact it and squeeze the molten magnesium and magnesium chloride out of the block. It is reported that the piston must develop a pressure of 2 to 12.5 kgf/cm<sup>2</sup> in order to produce a relatively dense titanium block containing 10-15% magnesium and magnesium chloride. It appears that this figure must be substantially increased in actuality. To prevent excessively strong cohesion with the titanium block, crystallizer 13 is slightly expanded downward (1:100).

During shaping of the titanium block, the bottom of the block is in close contact with solidifying layers of the fused salt bath, since the appropriate temperature is maintained here by cooling the bottom of the reactor. A thin crust of hardened salt forms between the bottom of the block and the inner surface of the crystallizer as a result of chilling by their surfaces.

To regulate temperature in the zone in which the pressed block is ejected from the reactor, one of the more recent patents<sup>(49)</sup> proposes that the crystallizer, which is attached at the bottom of the reactor, be provided with induction heating. Since the inductor takes the form of a coil through which cooling water can be passed, it serves as a cooler when switched off. Either the crystallizer wall or the compacted block of reaction mass is heated by high-frequency current, thus forming an interlayer of fused salt, which makes it easier to extract the block.

Patent<sup>(50)</sup> describes a combination of bubbling and pressing. The reactor is oval in shape, does not have the upper piston, and uses two vertical worms, which are so arranged as to clean the

Footnote (49) and (50) are on page 447.

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titanium product not only from the reactor walls, but also from one another, to transport the sponge downward and compact it. The worms are hollow and can be cooled with a liquid, such as titanium tetrachloride.

This reactor design would appear to be less successful than the version in which a piston is used for expression.

Patent<sup>(51)</sup> also describes a press for compacting the reaction products and their removal from the reduction apparatus. Titanium tetrachloride and molten magnesium are fed onto the surface of an internally cooled cone placed in the reactor in an inclined position. The cone is rotated slowly, with the result that reaction products that have stuck to its surface are passed under a press piston on one side of the cone, which moves vertically in contact with the generatrix of the cone. As it comes down, the piston strips the reaction mass from the surface of the cone into a bottom-opening drawing plate. The mass is compacted in this plate and expelled in the form of an extruded block.

To improve the cohesion of the extruded blocks of reaction mass, it has been proposed that the ram of the press be fitted with projections half as high as the layer of mass to be compacted.<sup>(52)</sup>

#### Reduction with Process Localized at the Center of the Reactor

A number of patents have proposed versions of the continuous process in which a block of reaction mass is grown in the center of the reactor. The reactor wall is vigorously cooled, and a liner builds up on it and prevents adhesion of the reaction-mass block to the wall. If the reduction reaction manages to take place at the inner surface of the liner in spite of its low temperature, it would appear that the resulting reaction mass would be unable to mesh with the liner surface.

Patent<sup>(53)</sup> proposes the apparatus shown in Fig. 78.

The reactor 1 is a double-walled cylinder with a cooling liquid between its walls. To prevent condensation of  $TiCl_4$ , the reactor's internal surface must be at a temperature no lower than

Footnotes (51), (52) and (53) are on page 447.

150°C. The tetrachloride is delivered through pipe 2 into reaction zone 3; magnesium is fed into the reaction zone through gland 4 in the form of rod 5. The reaction products form a block 6, the top of which is in the liquid bath 7, which consists of magnesium chloride and magnesium.

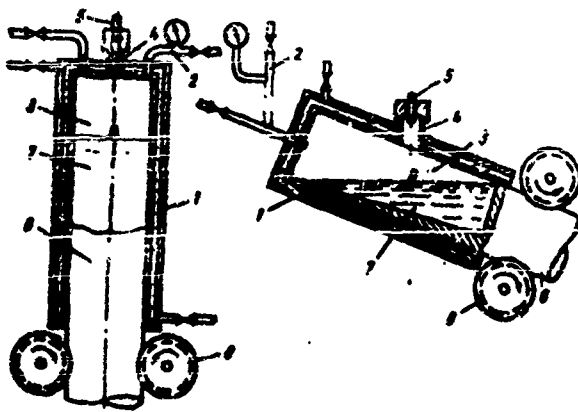


Figure 78. Diagram of apparatus for continuous titanium production with process localized at center of reactor.

To obtain a more compact reaction mass, the  $TiCl_4$  pressure in the apparatus is held in the 3-5-atm range. It is proposed that the shrinkage of the reaction-mass block as it chills will weaken its grip on the reactor inner surface and that it will sink under its own weight. Nevertheless, rolls 8 are provided for extraction of the block. The block is then heated to a temperature above the melting point of  $MgCl_2$ . Here, about 2/3 of the  $MgCl_2$  drains out and 1/3 is trapped by the titanium sponge. The magnesium chloride left in the block is removed by the conventional methods, e.g., vacuum distillation.

Note is taken of the advantages of inclining such apparatus: without changing the reactor diameter (which is essential for strong cooling of the reactor), the magnesium can be introduced at several points, since the surface of the melt in an inclined reactor is an ellipse. It is claimed that the specific

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productivity of the proposed reactor (per unit of reactor cross sectional area) could be 5-10 times higher than those of ordinary intermittent-process reactors.

It is reported in another similar patent<sup>(54)</sup> that the sponge forms in a circle whose diameter is several times the diameter of the original magnesium rod, since some of the molting magnesium manages to spread out over the surface of the magnesium chloride melt before it is entirely consumed by reduction. For this reason, the reactor diameter must be 5-6 times the diameter of the magnesium rod fed into it.

For the reaction to proceed at maximum speed, the end of the magnesium rod must remain at about 125-250 mm from the melt surface. Reducing or increasing this distance slows down the reaction.

The utilization of magnesium may range up to 97%, and the rate of titanium tetrachloride delivery up to 150 g/h per square centimeter of reactor cross section.

Patent<sup>(55)</sup> describes an apparatus of similar design but with a device for drainage of the magnesium chloride. The reactor (Fig. 79) has a cooled wall 1, on which a liner 2 is built up. The titanium tetrachloride enters through pipe 3, and the magnesium rod 4 is introduced through gland 5. To hold the level of the molten magnesium chloride constant in the reactor, the excess chloride is removed through externally heated drainage device 6, which is mounted just below the reduction zone. It is claimed that up to 90% of the magnesium chloride product can be removed from the reactor through this system. The block 7 of reaction mass is extracted from the reactor by rolls 8.

Footnotes (54) and (55) are on page 447.

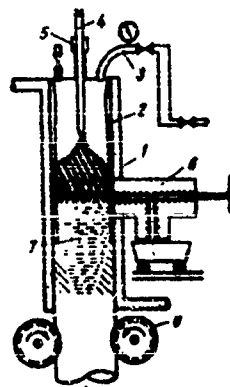


Figure 79. Diagram of apparatus for continuous titanium production with process localized at center of reactor and magnesium chloride drainage.

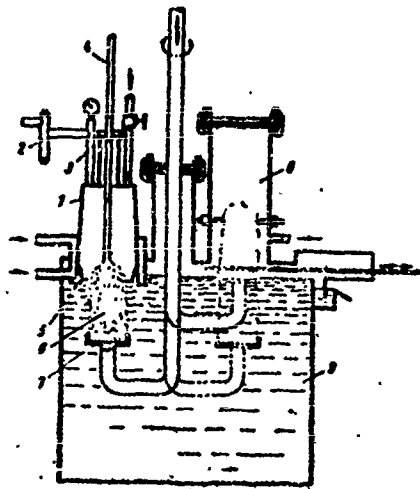


Figure 80. Diagram of apparatus for semicontinuous production of titanium.

5 on its surface. The reaction-mass block 6 is grown on cantilever support 7, which is lowered as the block grows. When the block has reached a certain height, support 7 is rotated to bring block 6 into cooling chamber 8. The bottom of the reactor is filled with liquid magnesium chloride 9.

A block of sponge 200-300 mm in diameter is obtained from a magnesium rod 30 mm in diameter. The level of the sponge above the melt is held constant by means of a radioisotope level gauge.

The patent claims that this reactor can be operated continuously if reaction-mass block 6 is extracted through the floor of the reactor.

The four patents discussed above provide for high rates of titanium tetrachloride reduction in the center of the reactor in the presence of a magnesium chloride liner on its inner surface. Rough calculations made by I.M. Rafalovich indicate that the liner on the reactor wall presents no significant obstacle to dissipation of the excess reduction-reaction heat from the reactor [309].

Footnote (56) is on page 447.

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The same patent proposes a variant of the reactor design, which is to be fed with a liquid reducing agent such as sodium.

Figure 80 presents a diagram of the bell-type reduction apparatus, whose design is based on the same principle of utilizing a liner layer to eliminate cohesion of the sponge with the inner surface of the reactor.<sup>(56)</sup>

The reduction reaction proceeds under bell 1, into which titanium chloride is fed through pipe 2 and the magnesium rod 4 through gland 3. The bottom of bell 1 is cooled to form liner

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With forced cooling of the reactor outer surface to comparatively low temperatures, e.g., 500°C and lower, a magnesium chloride lining forms on its inner surface. Its thickness will be determined by the temperature in the reaction zone and on the outer reactor surface, or, in other words, on the rate of dissipation of heat from the reactor. If for some reason, the reaction-zone temperature rises, the liner thickness will increase accordingly if the rate of reactor cooling is unchanged. Reducing the liner thickness accelerates transfer of heat through the reactor wall, i.e., it creates the requisites for lower reaction-zone temperature. Thus, the liner will to some degree stabilize temperature conditions in the reactor.

The liner will also form spontaneously even above the level of the magnesium chloride melt in the reactor, owing to condensation of magnesium chloride vapor and deposition of lower titanium chlorides along with the magnesium chloride.

According to a patent cited earlier<sup>(57)</sup> the purpose of draining magnesium chloride is to remove it more thoroughly from the block that is produced. Because of the presence of the drainage unit, the magnesium is delivered not onto the surface of the  $MgCl_2$  melt, but onto the titanium block projecting from it. Another patent<sup>(58)</sup> takes note of yet another advantage of this reduction method — the acceleration of the reduction process that results from its taking place on a vertical surface presented by the growing titanium block. Here the block is grown on the moveable support in such a way that the top of the block will at all times be above the fused-salt level.

It was shown experimentally in a study by V.A. Pazukhin and V.A. Shubin that removal of the chloride from the reduction-reaction zone increases the rate of this reaction [317].

One patent<sup>(59)</sup> also proposes that the reduction be carried out in a bell-type unit, but at a temperature above the boiling point of magnesium chloride, so that the magnesium and magnesium chloride impurities present in the "stalagmite" can be removed from it at once.

Footnotes (57), (58) and (59) are on page 447.

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The above designs of liner-type reduction reactors proposed as their basic variant delivery of the magnesium into the reactor in the form of grafted rods. It is assumed that the magnesium will melt in the reactor and react with the titanium tetrachloride as it spreads out over the surface of the magnesium chloride melt or the block of reaction mass. A patent mentioned earlier<sup>(57)</sup> notes that the magnesium can also be fed into the reactor in liquid form. The patent claims that the lower chlorides of titanium do not form in the reactor.

Another patent<sup>(60)</sup> mentions the need for periodic cleaning of the top of the reactor (above the melt) to remove the lower chlorides.

#### Reduction by Amalgams

Among the continuous methods that have been proposed for titanium production, those in which the titanium tetrachloride is reduced by an amalgam of the reducing metal form a class of their own. Patents have been issued in various countries for variations of this method, for example, to Kennecott Copper<sup>(61, 62)</sup> and Imperial Chemical Industries.<sup>(63, 64)</sup> This method has also been under development at a pilot plant in Austria [318, 319].

The patent proposals<sup>(61-63)</sup> recommend the reduction of  $TiCl_4$  at temperatures of 45-105°C with vigorous mixing of the reactants. To prevent formation of lower titanium chlorides, it is necessary that at least a twofold excess of sodium over stoichiometric be present in the reactor.

It should be noted that the possibility of single-stage reduction directly to the metal at temperatures around 100°C appears highly doubtful, since the formation of solid sodium chloride and lower titanium chlorides, as well as the dispersed form of the titanium produced, would have to interfere with reduction. This is confirmed by published results obtained in developmental work on the amalgam method [318, 319].

A number of improvements have been proposed<sup>(65)</sup> for the amalgam process: increasing the sodium content in the amalgam to 3-4.5%, introducing the amalgam into the reactor in vapor form, Footnotes (57), (60), (61), (62), (63), (64) and (65) are on page 447.

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holding the reactor temperature somewhat higher than 800°C so that the sodium chloride will be separated as a liquid, or conducting the process at about 1500°C to produce the sodium chloride as a vapor. The reaction products, which represent a mixture of mercury and sodium vapors, droplets of sodium chloride, and titanium particles in the former case or, in the latter case, vaporized mercury, sodium, and sodium chloride and titanium particles, are introduced into a cyclone housed inside the reduction apparatus for separation of the solid phase or the mixed solid and liquid phases from the gaseous phase. Then the titanium particles are separated from the sodium chloride either by filtration at temperatures above 800°C or by vacuum separation.

Configuring the process in which titanium tetrachloride is reduced by sodium amalgam as a continuous process does not improve it substantially, so that it would appear to have little chance of industrial application. Since the stage in which the titanium is extracted from the reduction-reaction products remains intermittent, the amalgam processes examined here would be more correctly termed semicontinuous.

#### Other Continuous Reduction Processes

In one proposal,<sup>(66)</sup> the reducing agent is granular magnesium from hopper 1 (Fig. 81), which batcher 2 sprinkles on internally cooled disk 3. The disk rotates at a linear velocity of about 3 m/min. The reactor is filled with  $TiCl_4$  vapor. After the time needed to heat the magnesium to the reaction temperature (710-850°C), it begins to interact with the  $TiCl_4$ . Since the magnesium is heated gradually, the reaction proceeds smoothly, the magnesium "glows," titanium sponge 4 forms on the disk, and the magnesium chloride drains to the bottom of the reactor for removal from the reaction zone.

An ejector placed in operation at periodic intervals removes the sponge from the disk, making room for a new portion of magnesium.

The authors of this patent underestimate the ability of  $TiCl_4$  to undergo reduction to the lower chlorides instead of the metal

Footnote (66) is on page 447.

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at comparatively low temperatures. Although it is claimed in the patent that this method of titanium production satisfies all requirements made of a continuous method, it is more probable that lower titanium chlorides will form preferentially under the conditions proposed.

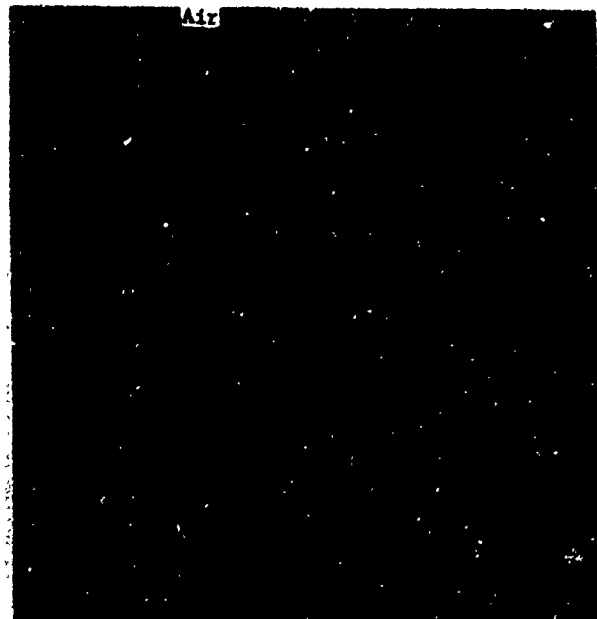


Figure 81. Diagram of equipment for continuous titanium production using granular magnesium.

Note must be taken of the inexpediency of one of the elements of the reactor shown in Fig. 81. The fragments of titanium sponge, from which a large part of the magnesium chloride has been removed, are dropped back into the magnesium chloride melt for subsequent extraction by worm 5.

The drum-reactor design<sup>(67)</sup> for which the British firm Imperial Chemical Industries has been awarded a patent is much better thought-out.

Footnote (67) is on page 447.

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The reactor (Fig. 82) is a horizontal or slightly inclined drum 1 in rotation at a comparatively low circumferential speed — about 20 m/min. The starting reactants — titanium tetrachloride and liquid sodium — are fed into the reactor through

hollow shaft 2 through two concentric pipes 3 and 4, with the central pipe 4 used for the so-

dium. It is noted in the patent that this method of delivering the starting reagents eliminates the possibility of reduction products building up on the ends of the feeder pipes, since, in the event that titanium sponge is deposited on the end of either pipe 3 or 4, this sponge reacts immediately with the excess  $TiCl_4$  to form lower titanium chlorides, which can be washed into the bottom of the drum for further reduction to the metal.

Since the drum is rotated, the titanium sponge forms as 15-20-mm granules, which do not adhere to the inner surface of the drum and are removed from it together with the sodium chloride through "scroll" 5, which is fitted to the second hollow shaft 6.

It is stated that since the reaction zone in this unit is comparatively large, it is highly productive: 60 kg of titanium per hour at a diameter of 1200 mm and a length of 600 mm.

The external gas heating system of the reactor is switched on during the initial phase of its operation.

To improve the interaction between the reactants, the drum is divided by partitions 7 into several compartments. In addition, rectangular bars 8 are secured to the inner surface of the drum in each of these compartments. Thus, as the drum rotates, the liquid phases overflow from ledge to ledge and are thoroughly mixed and transported from one compartment to the next in the direction of the exit shaft.

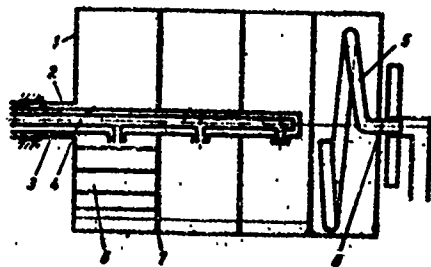


Figure 82. Diagram of drum-type apparatus for continuous titanium production.

The patent claims that not only sodium, but also magnesium, which can be delivered in liquid form or in small fragments through the same hollow shaft 2, can be used as the reducing agent.

This drum reactor has a number of interesting features: continuous renewal of the reducing-metal surface, which may give a rather high reduction rate owing to the large area of the reaction zone; production of the metal in the form of granules makes it easier to process them later, as by mixing with alloying additives and pressing into consumable electrodes.

However, it is reported in a later patent<sup>(68)</sup> awarded to the same firm that difficulties had arisen in operation of this unit: periodic formation of very large titanium aggregates that would not fit into the exit pipe. The suggestion offered to correct this effect was to reduce the rate of reducing-agent delivery into the reactor at periodic intervals, thereby promoting the reaction between titanium tetrachloride and titanium, which results in smaller sizes of the aggregates. This procedure could hardly be regarded as rational, since the titanium tetrachloride would react not only with the large aggregates of the metal, but also — and apparently with even greater rapidity — with the smaller ones.

The widespread use of the plasma jet gives rise to the question as to whether it might be used to produce titanium. It is theoretically possible to heat the starting material, e.g., titanium tetrachloride, to its dissociation temperature in a plasma jet. However, as is correctly observed in a study devoted to application of plasma heating in metallurgy [325], the basic difficulty will be prevention of the reverse reaction in which titanium chlorides are formed as the dissociation products are subsequently cooled.

The reaction in which magnesium oxide is reduced by carbon at 2000°C with formation of gaseous products — magnesium vapor and carbon monoxide — was accomplished on an industrial scale as long as about 30 years ago. When these products were cooled slowly, the reverse reaction went to 100% completion. However, "quenching" of the same mixture with cooling to a temperature

Footnote (68) is on page 447.

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below 200°C within thousandths of a second made it possible to produce extremely fine magnesium powder in a yield of about 90%.

The higher the temperature of a plasma process, the larger will be the amount of coolant required for instant lowering of the temperature of the titanium-chloride dissociation products to a value at which the reverse reaction no longer occurs. As in the production of magnesium by this method, processing the extremely fine titanium powder into compact metal will give rise to considerable difficulty. In the case of magnesium, this was accomplished by the use of a complicated and expensive periodic sublimation method, since it was impossible to remelt the extremely fine dust; this process is not suitable for titanium, and it would be necessary to seek other ways.

Patent<sup>(69)</sup> proposes reduction of titanium tetrachloride by atomic hydrogen at a temperature above 3500°C. The burner is fed a mixture of hydrogen with titanium tetrachloride. The liquid titanium that is formed is absorbed in a liquid-titanium bath confined in a titanium liner. The hydrogen chloride produced in this reaction is delivered to a heat exchanger and thence to users or for neutralization. It is doubtful whether this process could be used in practice.

Thus, substantial technological and design difficulties must be overcome before the presently known high-temperature titanium-producing processes become a practical reality.

#### Extraction of Titanium from Reaction Mass

A number of patents have proposed that the products extracted from continuous-duty reactors be processed into the metal by conventional methods. However, vacuum separation of the reaction mass is an extremely expensive, intermittent, and unproductive process. Its use brings to naught the advantages gained by continuous reduction. Ordinary leaching of the reaction mass is also irrational, since acceleration of the reduction process often produces dispersed titanium, which undergoes rapid oxidation during leaching. Thus, new or improved methods for extracting the titanium from the reduction products must be sought along with

Footnote (69) is on page 448.

continuous-reduction technologies.



Figure 83. Diagram of unit for increasing size of titanium particles in reaction mass by heating them with high-frequency current. 1) Supply of initial material and argon; 2) sintering zone; 3) inductors; 4) heat-treatment zone; 5) heat and electrical insulation; 6) cooling zone; 7) water jacket; 8) sintered block of reaction mass.

with the furnace wall. In the upper zone of the furnace, the titanium particles are sintered at 900°C into a block that is heated

Footnotes (70), (71), (72), (73), (74) and (75) are on page 448.  
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To accelerate vacuum separation, it is recommended that the process be run at temperature above the boiling points of magnesium chloride (1418°C) and sodium chloride (1465°C). It is proposed that either graphite drip pans placed in a tunnel furnace<sup>(70)</sup> or a vibration conveyor in the furnace<sup>(71)</sup> be used for this purpose. In view of the need for holding the material being processed at 1500-1700°C, the practical value of these proposals is highly doubtful.

Proposals calling for refining of the reaction mass by leaching with preliminary high-temperature holding to aggregate and passivate the titanium particles are more rational.

To aggregate the titanium sponge, it is recommended that the reaction mass be heated briefly in a graphite retort<sup>(72)</sup> to 1400°C with subsequent leaching.<sup>(73)</sup>

High-frequency heating<sup>(74, 75)</sup> is more rational for this purpose. The dispersed reaction mass is loaded into a vertical high-frequency furnace (Fig. 83) fitted with two inductors: an upper inductor for low-temperature heating, and a lower one for heating to 1500-1700°C. The diameter of the upper zone is 100 mm, and that of the lower zone 150 mm to eliminate the possibility of the titanium block coming into contact

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to 1600-1650°C in about three minutes in the lower zone. The productivity of a furnace with these dimensions is about 20 kg of titanium per hour. The specific surface area of the titanium is reduced from 0.22 to 0.04 m<sup>2</sup>/g as a result of the treatment described.

The unit described in patent<sup>(76)</sup> operates on a similar principle. It is reported that the titanium particles, rather than the salt, which is not electrically conductive, are heated preferentially in a high-frequency field. The temperature of the titanium particles may reach 1600-1700°C, i.e., their melting point, within a few seconds. The temperature of the salt surrounding the titanium particles rises only from 750 to 910°C during this time. As a result, the specific surface area of the titanium can be reduced by a factor of about 20 — from 0.4 to 0.02 m<sup>2</sup>/g.

According to these patents, the electric power consumed for the operation is about 1.5 kW·h/kg.

Obviously, the surface-melted or thoroughly sintered titanium particles can be separated from the solid salt with no particular difficulty.

Interest attaches to the report discussed in Chapter 12 on industrial-scale application of continuous leaching to magnesiothermic reaction mass in an inclined rotating drum 2.44 m in diameter and 20.2 m high at the TMCA titanium plant at Henderson [327]. It is reported that the operating cost of the leaching process was reduced 30% on transition to the continuous process. Before the industrial apparatus was built, experiments were run on glass models, and a semiindustrial installation 12 m long and 1.2 m in diameter was tested.

A patent discussed earlier<sup>(77)</sup> proposed that the reaction mass be extracted from the reduction apparatus as a consumable electrode for arc-furnace melting. No data have been published on the use of this proposal in titanium production.

However, it has been reported that this technology is used to produce zirconium [314]. The zirconium is obtained as a fine

Footnotes (76) and (77) are on page 448.

powder with particle sizes no greater than 30  $\mu\text{m}$  in a reactor 150 mm in diameter. Nevertheless, pressing is successful and produces a block containing 91% zirconium, 3% reducing metal, and 6% salts. The density of the block is about 85% of the density of zirconium. The impurities present in the block (reducing metal and salts) are for the most part in its outer layers and are removed by skinning it on a machine. Nipple joints are cut into the block simultaneously, and it goes directly for remelting in a vacuum arc furnace, where it is used as a consumable electrode. Because of the volatile inclusions present in the block, the arc furnace is fitted with a heavier-duty vacuum system and traps for the vapors of the reducing-agent and salt impurities. A second remelting of the ingot is carried out under ordinary conditions.

It is noted in [314] that the continuous process makes it possible to obtain zirconium (titanium) of high purity with constant impurity content and composition. Alloying components for production of alloys are loaded into the reactor, which also takes scrap. For example, the alloy "Zircalloy 2," which contains several alloying additives, has been produced in this way.

A larger, industrial reactor 200 mm in diameter was built later, also for zirconium production. This reactor was found to be four times more productive than the conventional intermittent-type industrial reactor [315].

The claim that an arc furnace had been used successfully to melt consumable electrodes containing only 91% of the metal was received with certain reservations, since it is known that even a relatively small increase in chloride content in titanium sponge complicates the titanium-remelting process when ordinary vacuum arc furnaces are used.

Indeed, it became known two years later that persistent attempts to adapt arc melting for consumable electrodes containing, in addition to zirconium, 10-15% of volatile impurities — the reducing metal and its chloride — had met with failure. Before melting, consumable electrodes produced by direct pressforming of

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reaction mass had to be vacuum-separated to reduce their volatile content from 15-20% to 0.6% [321]. Thus, it had not been possible to design a continuous industrial zirconium production process; the process was in fact semicontinuous, although it still had a number of advantages over the intermittent process.

The technology described above for continuous zirconium production was thoroughly tested on the laboratory scale [326]. Conditions under which pressformed blocks containing 90% of the metal and 10% of the salt were established. As would be expected, attempts to melt such blocks in an arc furnace resulted in spattering of the metal and extinction of the arc.

It is obvious that arc-furnace designs for remelting of consumable electrodes containing substantial quantities of volatile substances must make provision for the inevitable spattering of droplets of the melting metal that results from the formation of large amounts of reducing-metal and chloride vapor during melting. One of the patents<sup>(78)</sup> describes such an arc-furnace design (Fig. 84). It has a water-cooled casing 1 into which the consumable electrode 2 is introduced. The other pole is the cooled table 3, which is turned by electric motor 4. The drops of titanium 5 formed on melting drop onto table 3, from which they are slung by centrifugal force. On striking the cold wall of the furnace casing 1, the drops freeze into beads that drop to the bottom of the furnace, from which they are extracted through unloader 6. The volatile impurities — magnesium and magnesium chloride — are deposited as a solid condensate 7 at the top of the furnace. This condensate is removed when the furnace is opened before the next melting operation.

Patent<sup>(79)</sup> proposes a furnace of somewhat different design (Fig. 85). The consumable electrode 1 is introduced into furnace 2 from the side. The second pole is rotating drum 3, which is made of titanium; the liquid used to cool it enters and leaves through the hollow shafts 4. The titanium droplets freeze in flight into spherical granules 5. Consumable electrodes for the remelting that follows are made from these beads by sintering with electric current. It is reported that the volatile content

Footnotes (78) and (79) are on page 448.

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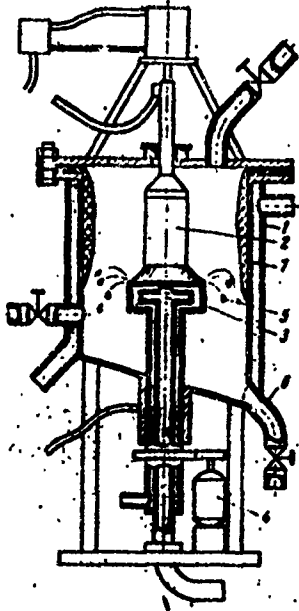


Figure 84. Diagram of arc furnace with turntable for melting consumable electrodes containing volatile components.

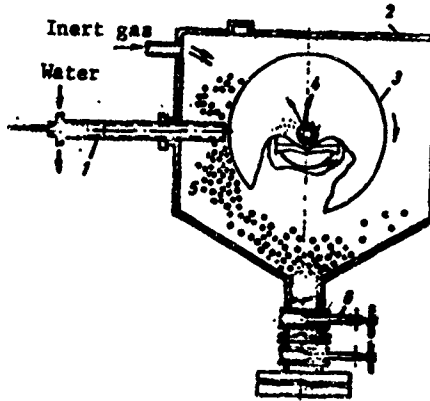


Figure 85. Diagram of arc furnace with rotating drum for melting consumable electrodes containing volatile components.

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Patent<sup>(80)</sup> reports that the sodium chloride content of the consumable electrode may not exceed 15%, since otherwise it loses mechanical strength. To produce the consumable electrodes, the reaction mass is rolled at 900°C in steel containers with perforated partitions to separate the salt from the metal. The patent does not indicate methods for melting these electrodes.

Titanium consumable electrodes containing volatile impurities may also be melted by induction in a water-cooled copper crucible consisting of four segments that are electrically insulated from one another.

A coating of electrically nonconductive refractory material, such as aluminum oxide, is applied to the inner surface of this

Footnote (80) is on page 448.

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in the consumable electrode for this furnace may range up to 50%. Melting takes place in an inert-gas atmosphere. The titanium granules and the condensed particles of the volatile impurities are unloaded from the fur-

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crucible with a plasma arc. This reduces the danger of shorting between crucible segments through the metal in the crucible and substantially reduces losses of heat from the crucible, but it may result in oxygen contamination of the titanium. The crucible may be bottomless, in which case it becomes a crystallizer from which the ingot is drawn [322]. Since there is no arc in this furnace, vaporization of volatile impurities cannot interfere with the melting process.

Patent<sup>(81)</sup> describes a high-frequency furnace for melting of consumable electrodes made from reaction mass. The bottom end of the consumable electrode is introduced into the inductor of a high-frequency (10 kHz) installation and melts in it. The drops of metal strike a turntable, impingement on which converts them into irregularly shaped granules, which are subsequently easily pressed into a consumable electrode for conventional melting. A neutral gas is passed through the melting space to carry away the reducing-metal and chloride impurities released from the consumable electrode and carry them to a condenser.

It has been proposed<sup>(82)</sup> that titanium be melted in a resistance furnace with an ordinary copper crystallizer and a conical graphite heater that develops temperatures up to 2600°C (see Chapter 20).

The above exposition indicates that two possibilities for stepping up the refinement of reaction mass obtained by continuous reduction are presently of greatest interest: heat treatment of the reaction products for aggregation and passivation of the titanium particles with subsequent leaching, or pressing of consumable electrodes from the reaction mass and melting them in specially designed furnaces. Methods for alloying of the titanium to produce final alloys must be developed for the latter method.

#### Prospects for the Development of Continuous Methods

The wide variety of these directions being taken by the development of continuous titanium production processes indicates the great amount of attention being devoted to this problem.

Footnotes (81) and (82) are on page 448.

Despite the present slowdown in the titanium industry of capitalist countries, reports on the development of continuous titanium production processes and corresponding patents continue to appear just as frequently as during the headlong development of this industry. Until very recently, however, no reports were published on the development of an industrial continuous metal-thermic process for titanium production.

As we noted in Chapter 1, the firms Kennecott Copper and Allied Chemical and Dye combined forces in 1956 to build a 7500-ton-per-year sodiothermic plant at Wilmington, North Carolina; they proposed to use a continuous sodiothermic process at this plant. Construction work at this plant was suspended when the American titanium industry began to stagnate.

At about the same time, Reactive Metals began to build a sodiothermic plant at Ashtabula, Ohio, which was also supposed to be based on a semicontinuous sodiothermic process. This plant was placed in operation at the end of 1959, and it was reported that it performed successfully and began to produce commercial metal.

A two-stage continuous sodiothermic process was developed in 1956 at the US Bureau of Mines experimental station at Boulder City [323].

Finally, a report published in 1966 stated that developmental work on a continuous sodiothermic titanium production process had been completed at the Ashtabula plant.

The above reports were not accompanied by any details on the flowcharts and equipment designs that had been adopted. Characteristically, all of them refer to the development of a continuous sodiothermic titanium production process.

It appears that the design of a continuous magnesiothermic process is a more difficult problem. Early in this chapter, we enumerated the advantages of sodium over magnesium as a continuous-process reducer. However, the reported industrial-scale realization of a continuous process for leaching magnesiothermic titanium sponge will make magnesium more competitive with respect

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to sodium, since it will to a substantial degree offset one of the most important and, as we have noted, peculiar advantages of sodium: the possibility of leaching out the reaction mass instead of vacuum-separating it. It should be noted that magnesium also has a highly important economic advantage as a reducing agent for a continuous titanium tetrachloride reduction process. It consists in the fact that most titanium is now produced by intermittent magnesiothermic processes and conversion of these plants for continuous magnesiothermic production would present no particular difficulty.

It is hardly necessary to point out that from this standpoint, prospects for the introduction of a continuous sodiothermic process are less favorable, since it could be used only at a few existing sodiothermic plants whose flowcharts are intermittent and at newly built plants.

It is also necessary to note that magnesium also has technological advantages over sodium — a substantially lower vapor pressure, which makes it easier to eliminate the undesirable gaseous-phase reduction reactions, and stability in ordinary atmospheres, which is important for direct acquisition, in the reactor, of reaction-mass blocks that can later be used as consumable electrodes in smelting out titanium ingots.

In conclusion, a few words on the economics of continuous metallothermic titanium production are in order. It has been suggested that introduction of a continuous process would introduce no substantial changes in the net cost of the titanium, since (in the case of the intermittent process), half the cost is that of the titanium tetrachloride, which will not change as a result of the new technology [306]. This conclusion is unjustified, since the improvement of titanium tetrachloride production technology should reduce its representation in the cost of the titanium substantially; introduction of the continuous metallothermic process will result in substantially lower direct costs, and, in particular, reduced specific capital investment and, consequently, depreciation writeoffs; labor costs will also be reduced. It is also necessary to remember that introduction of the continuous process

should improve the yield of the higher, i.e., more expensive grades of titanium.

We should stress once again that even substitution of continuous for intermittent leaching of the reaction mass would result in substantial savings.

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Symbol List

| Manu-<br>script<br>Page<br>No. | Russian | When<br>Typed | Meaning |
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| 412                            | тв      | s             | solid   |
| 412                            | газ     | gas           | gaseous |

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Part V

REFINEMENT OF TITANIUM BY THERMAL  
DISSOCIATION OF HALIDES

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## Chapter 18

### GENERAL INFORMATION ON THERMAL DISSOCIATION OF HALIDES

We have noted that despite the substantial quality improvement achieved in recent years, technical titanium produced by metallothermic reduction of titanium tetrachloride contains a number of impurities that have a strong influence on its properties. At the same time, it is known that highly pure metals often exhibit new and highly valuable properties. Thus, interest attaches to improving the purity of titanium in every possible way.

The purer metal required for vacuum engineering and special applications, as well as for scientific research, is obtained by refining technical titanium. The method that has been best developed for this purpose is thermal dissociation of titanium halides, which yields titanium of increased purity in compact bar form.

The essentials of the method are as follows: the crude metal to be purified (technical titanium sponge or shavings) is treated with a halogen to form a volatile halide, which then dissociates on an electric-current-heated surface, usually a wire or ribbon of titanium or a refractory metal (tungsten, molybdenum). In this process, the titanium present in the halide is deposited on the incandescent wire, and the halogen that has been released is recycled to form a new batch of halide, which is again decomposed on the wire, on which the titanium bar is gradually grown.

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The following requirements must be taken into consideration in selecting the halogen most suitable for purification of titanium by this method [1, 2]:

- a) the halogen must form a sufficiently volatile halide with the metal to be refined;
- b) this compound (the halide) must be formed at comparatively low temperatures;
- c) the decomposition temperature of the halide must be below the melting point of the metal being refined;
- d) the metal being refined may not have a high vapor pressure at the temperature at which it is deposited on the wire;
- e) the rate of decomposition of halide and deposition of the metal on the glowing wire must be substantially higher than the rate of its evaporation.

Although all halogens form volatile compounds with titanium, its iodides are usually used in refining this metal by thermal dissociation; as a result, the method has come to be known as the iodide process. Iodine is preferred over the other halogens because, as we shall show below, it reacts most readily with titanium and at lower temperatures, and the iodides that are formed dissociate practically completely on the incandescent surface (wire, ribbon, etc.) into titanium and iodine, even at comparatively low temperatures (of the order of 1100-1400°C), at which the metal's vapor pressure is still moderate. On the other hand, the decomposition temperatures of titanium chlorides and bromides are substantially higher than those of the iodides, so that it becomes difficult to use these two halogens in this process [3, pages 46-58]. The same applies to the fluorides, which are highly toxic and, like the chlorides and bromides, less thermally stable than the iodides of titanium.

Reduction of titanium bromide by hydrogen on a glowing filament was proposed by the firm Osram in 1915. Although bromine is substantially cheaper than iodine and no difficulty is encountered in forming titanium tetrabromide from titanium carbide and bromine,

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the bromide method was not put to practical use. The method requires an extremely large hydrogen excess, and the hydrogen must be highly purified to avoid contamination of the metal product. The bromide process is further complicated by the need to regenerate the bromine from hydrogen bromide and by the formation of lower titanium bromides, with which bromine is lost.

The iodide method is applicable for purification of a number of elements — titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, chromium, boron, silicon, and certain others [2]. The method was first proposed by Van Arkel and de Boer in 1925 [4], and was subsequently developed further in the work of these authors, as well as by Fast and many other investigators [5-9].<sup>(1)</sup> The early papers recommended that the refractory metals, including titanium, be deposited onto an electric-current-heated surface from their volatile halides in the presence of hydrogen or some other gaseous reducing agent.<sup>(2)</sup> Reducing gases were later abandoned, thus making it possible to eliminate the impurities that they introduced.

Purification of crude (technical) titanium by the iodide method is based on the difference between the vapor pressures of the titanium iodide that is formed and the iodides of the impurities present in the metal. Moreover, not all of the impurity elements present in technical titanium form iodides. This makes it possible to purify the titanium quite effectively of the impurities that are not bound into iodides or form nonvolatile or thermally unstable iodides (for example, owing to its low thermal stability, titanium oxyiodide does not transfer to the incandescent filament, and this makes it easier to remove the oxygen impurity from the titanium).

Iodination is the decisive stage from the standpoint of purifying titanium, since the volatile iodides are decomposed on the glowing wire in the second stage with formation of the bar of the metal, whose impurity content usually corresponds to the purity of the titanium iodide vapor. This is because the iodides of the principal impurities present in the titanium decomposed at temperatures below the optimum dissociation temperature of

Footnotes (1) and (2) are on page 484.

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titanium tetraiodide (about 1400°C) [10]. Below we present the decomposition temperatures of the iodides of certain elements in °C:

|                   |      |                    |      |
|-------------------|------|--------------------|------|
| Chromium. . . . . | 1100 | Silicon. . . . .   | 1000 |
| Copper. . . . .   | 900  | Vanadium . . . .   | 1200 |
| Iron. . . . .     | 1100 | Titanium . . . . . | 1400 |
| Nickel            | 1030 |                    |      |

A deficiency of the iodide method is its low productivity. This is basically why iodide titanium is several times more expensive than the technical grade.

**Reaction of Titanium with Iodine and Iodides**

Iodine is a crystalline substance of orthorhombic structure with lattice constants  $a_0 = 4.795 \text{ \AA}$ ,  $b_0 = 7.255 \text{ \AA}$ , and  $c_0 = 9.780 \text{ \AA}$ ; it has a density of  $4.94 \text{ g/cm}^3$  (at 18°C). Its melting and boiling points are 113.6 and 184.4°C, respectively [2]. The temperature curve of the pressure of iodine vapor above solid iodine can be represented by the equation [11]

$$\lg P_{\text{mm}} = \frac{-3512.8}{T} - 2.013 \lg T + 13.374.$$

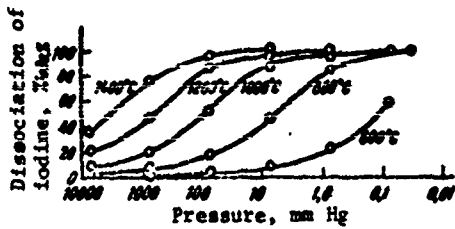


Figure 86. Degree of dissociation of iodine as functions of temperature and pressure.

Gaseous iodine dissociates more readily than do the other halogens, and the heat effect of the dissociation  $I_2 \rightarrow 2I$  is 35,514 cal/mole. Marked dissociation of iodine begins at 600°C under atmospheric pressure; it is 5.2% at 800°C, 19.7% at 1000°C, and 78.4% at 1400°C. As the isotherms shown in Fig. 86 [2] indicate, iodine dissociates substantially more rapidly with decreasing pressure.

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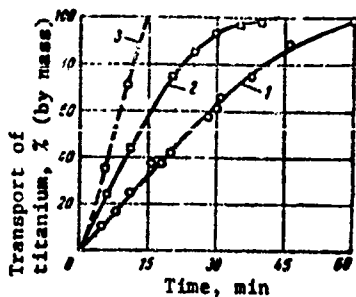


Figure 87. Rate of transport of titanium in the form of its tetraiodide at 175 and 400°C. 1) 175°C; 2) 400°C; iodine vapor pressure 25 mm Hg; 3) rate of distillation at 200°C.

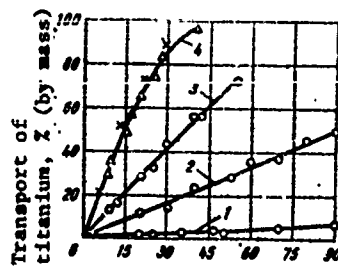


Figure 88. Influence of iodine vapor pressure  $p_{I_2}$  mm Hg, on the transport rate of titanium in the form of its tetraiodide. 1) 4; 2) 5 ( $t = 200^\circ\text{C}$ ); 3)  $\times - 25$ ;  $\Delta - 100$ .

Titanium tetraiodide, a hygroscopic reddish-brown crystalline substance — can be prepared by direct reaction between iodine and titanium at 170–200°C or by disproportionation of lower titanium iodides [12]. Thus,  $TiI_2$  and  $TiI_4$  are formed by heating solid  $TiI_3$  to 350°C in a vacuum, while heating  $TiI_2$  to 480°C in a vacuum produces  $Ti$  and  $TiI_4$ . The authors of other papers also prepared titanium tetraiodide by disproportionation of  $TiI_3$ . For example, Campbell and Kessler patented an improved process for the production of titanium tetraiodide by the reaction between metallic titanium and iodine; according to the patent, continuous cooling is used to remove reaction heat and stabilize temperatures in the reaction zone, and the condensing  $TiI_4$  flows as a liquid product through the metal to be iodinated, cooling it, and is collected in a receiver, in which it freezes.<sup>(3)</sup>

Runnals and Pidgeon [13] studied the rates of formation of the tetraiodide and its transfer to the wire in the reaction of iodine with metallic titanium (powder with grain size around 0.4 mm). The transport rates of titanium tetraiodide at 175 and 400°C and an iodine vapor pressure of 25 mm Hg are presented

Footnote (3) is on page 484.

graphically in Fig. 87. The dashed line indicates the rate of  $TiI_4$  distillation at 200°C. Figure 88 shows the influence of iodine vapor pressure (in the range from 1 to 100 mm Hg) on the transport rate of titanium tetraiodide at 200°C.

We see from Figs. 87 and 88 that the rate of titanium tetraiodide formation is quite high and increases with increasing iodine pressure and temperature.

Titanium triiodide is a dark violet solid and can be prepared by reacting  $TiI_2$  with  $TiI_4$  [14] or  $TiI_4$  with Ti at 300-340°C, as well as under other conditions, which are described in the literature [2].

Titanium diiodide is a dark brown solid, and was prepared by Fast [12] by the reaction of Ti with  $TiI_4$ . At 550°C, the  $TiI_2$  was obtained in a mixture with Ti. Heating this mixture to 750°C formed a mixture of three compounds: the di-, tri- and tetraiodides. Heating this mixture to 440°C caused disproportionation of the  $TiI_3$  into  $TiI_2$  and  $TiI_4$  and separation of the  $TiI_4$  from the diiodide, which has a low vapor pressure at this temperature.

$TiI_2$  has also been prepared by reacting  $TiI_4$  with titanium under other temperature conditions [15].<sup>(4)</sup>

Comparatively recently, Japanese investigators [16] made another detailed study of the conditions under which metallic titanium reacts with iodine and the resulting titanium tetraiodide reacts with the metal.

Contrary to earlier literature references to reactions between metallic titanium and iodine even at room temperature [17], the authors of this work established in a study of the iodine vapor pressure variations over titanium sponge at various temperatures that the reaction begins to proceed vigorously with formation of  $TiI_4$  only at temperatures above 130°C.

As indicated by the data in Table 39,  $TiI_4$  has a relatively low melting point (as low as 150°C). At these temperatures, the vapor pressure above solid  $TiI_4$  is negligible. The vapor pressure above  $TiI_4$ , according to the Japanese authors, can be determined from the empirical formula

Footnote (4) is on page 484.

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TABLE 39  
 Certain Physicochemical Properties of Titanium Iodides

| Iodide           | Physical state | $-\Delta H_{298}^{\circ}$<br>kcal/mole | $\Delta_{298}^{\circ}$<br>kcal/mole | Melting point, °C     |
|------------------|----------------|--|-------------------------------------|-----------------------|
| TiI <sub>2</sub> | S              | 102.0 <sup>*1</sup> [41]               | 64.6 <sup>**</sup> [23]             | 150 [20]              |
| TiI <sub>3</sub> | S              | 70.0 [23]                              | 102.4 [22]                          | —                     |
| TiI <sub>4</sub> | S              | 80                                     | 46.0 [21]                           | 900 [2]               |
| TiI <sub>4</sub> | S              | 62.5 [20] <sup>**</sup>                | 36.0 [20] <sup>**</sup>             | Sublimes <sup>6</sup> |
| TiI <sub>4</sub> | S              | -3.3 [23]                              | 72.5 [23]                           | —                     |

| Heat of fusion, kcal/mole | Boiling point, °C                                | Heat of evaporation, kcal/mole | Heat of sublimation, kcal/mole | Density, g/cm <sup>3</sup> |
|---------------------------|--|--------------------------------|--------------------------------|----------------------------|
| 4.4 [20]                  | 377 [2]  | 13.4 [20]                      | 20.5 [20]                      | 4.6 <sup>1</sup>           |
| —                         | —  | —                              | —                              | —                          |
| 8.4 [23] <sup>**</sup>    | 800 [2] <sup>**</sup><br>1420 [23] <sup>**</sup> | —                              | 56.3 (53.2)                    | 4.76 [4,94]<br>5.0         |

- \*1100 according to [20] and 92.2 according to [23].
- \*\*262.2 according to [20] and 61.8 according to [2].
- <sup>3</sup>At 0.01 mm Hg.
- <sup>4</sup>61 according to [2] and 47 according to [23].
- <sup>5</sup>37 according to [2].
- <sup>6</sup>850 according to [23] and 1050 according to [2].
- <sup>7</sup>6 according to [2].
- <sup>8</sup>1350 according to [2].

$$\lg P_{\text{vap. cm.}} = \frac{-3.06}{T} \cdot 10^3 + 7.57 \quad (2)$$

or

$$\lg P_{\text{cm.}} = \frac{-3.06}{T} \cdot 10^3 + 4.09 \quad (3)$$

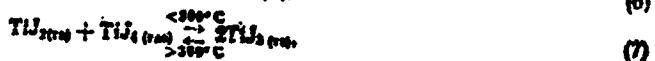
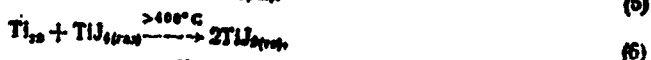
which agrees well with the empirical formula proposed by Blocher and Campbell [18]:

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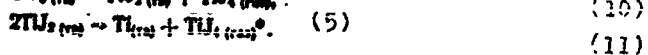
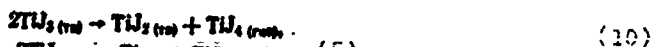
$$\lg P_{\text{I}_2} \text{ mm. Hg.} = -\frac{3064}{T} + 7.5773. \quad (4)$$

TiI<sub>2</sub> is formed at an acceptable rate in the reaction of TiI<sub>4</sub> with metallic titanium at temperatures above 400°C [15]. In the presence of an excess of the tetraiodide, titanium diiodide may react with it (at temperatures of 300°C or lower) with formation of TiI<sub>3</sub>.

It was established in [16] that in the presence of an excess of metallic titanium, the diiodide reacts with it to form the monoiodide TiI. Thus, there are four iodides in the titanium-iodine system: TiI<sub>4</sub>, TiI<sub>3</sub>, TiI<sub>2</sub>, and TiI, whose interaction and mechanism of formation can be represented by the following equations:



It is reported in [17] that TiI<sub>3</sub> and TiI<sub>2</sub> begin to disproportionate at temperatures above 350 and 480°C, respectively, in accordance with the equations



There are indications in the literature [15] that the latter reaction is the determining one for the titanium-iodine system at pressures of 3-15 mm Hg and a filament temperature of 1500°C, and that the equilibrium constant under these conditions equals  $8.2 \times 10^{-2}$  atm and  $\Delta Z^\circ = 8.6$  kcal/mole. However, in an experimental test of the first of these equations, Japanese investigators showed that the disproportionation reaction mechanism of the diiodide should be represented by the equation

Footnote (5) is on page 484.



and that the titanium monoiodide that forms disproportionates, in turn, according to the reaction



The equilibrium  $\text{TiI}_4(\text{gas})$  pressures that correspond to the above disproportionation reactions, and the theoretical  $\Delta Z^\circ$ ,  $\Delta H$ , and  $\Delta S$  are as follows [16]:

for Reaction (10):

$$\lg p_{\text{max. em.}} = -\frac{2.76}{T} \cdot 10^3 + 6.16, \quad (14)$$

$$\Delta Z^\circ = 12.7 \cdot 10^3 - 15.0 T \text{ cal/2 moles TiI}_2, \quad (15)$$

$$\Delta H = 12.7 \cdot 10^3 \text{ cal/2 moles TiI}_2,$$

$$\Delta S = 15.0 \text{ cal/(deg. 2 moles) TiI}_2;$$

for Reaction (12):

$$\lg p_{\text{max. em.}} = -\frac{3.24}{T} \cdot 10^3 + 6.24, \quad (16)$$

$$\Delta Z^\circ = 14.8 \cdot 10^3 - 15.47 T \text{ cal/3 moles TiI}_2,$$

$$\Delta H = 14.8 \cdot 10^3 \text{ cal/3 moles TiI}_2,$$

$$\Delta S = 15.4 \text{ cal/(deg. 3 moles) TiI}_2;$$

for Reaction (13):

$$\lg p_{\text{max. em.}} = -\frac{10.00}{T} \cdot 10^3 + 11.03, \quad (18)$$

$$\Delta Z^\circ = 48.9 \cdot 10^3 - 37.3 T \text{ cal/4 moles TiI}_2, \quad (19)$$

$$\Delta H = 48.9 \cdot 10^3 \text{ cal/4 moles TiI}_2,$$

$$\Delta S = 37.3 \text{ cal/(deg. 4 moles) TiI}_2.$$

The above empirical formulas permit approximation determination of the titanium tetraiodide vapor pressure in the reaction space for various temperature conditions, as will be shown below, this vapor pressure has a decisive influence on productivity in the iodide refinement of titanium.

Table 39 lists certain physicochemical parameters of titanium iodides according to [2, 20-22].

### Modifications of the Iodide Process

As we indicated above, various reactions may take place, depending on the conditions under which the technical titanium is iodinated. Thus, when titanium reacts with iodine at 175-200°C, the product is titanium tetraiodide, which dissociates on the hot wire by the reaction



If the titanium is iodinated at temperatures above 200°C, a secondary reaction begins to develop: that of titanium tetraiodide with titanium, which forms the diiodide:



At temperatures between 200 and 450°C,  $\text{TiI}_2$  has low vapor pressures, so that the rate of deposition of the metal on the wire slows down considerably [17]. In the case of work at low temperatures, therefore, it is necessary to watch temperature conditions carefully in order to prevent formation of lower titanium iodides. At higher temperatures (around 550°C), on the other hand, titanium diiodide is, as noted by Fast and other researchers [17, 24], volatile enough to replace titanium tetraiodide as the bearer of the metal and deliver a satisfactory rate of deposition of the metal on the hot wire.

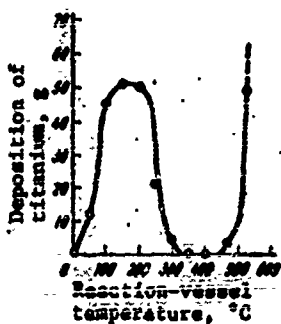


Figure 89. Rate of titanium deposition on wire as a function of temperature in reaction vessel.

This relationship was confirmed convincingly by Fast [17], who studied the influence of reaction-vessel temperature on the rate of deposition of titanium on the wire. The results of experiments conducted in a small Pyrex flask (charge: 80 g of crude titanium sponge, 25 g of iodine; heating filament: tungsten, 40  $\mu\text{m}$  long and 40  $\mu\text{m}$  in diameter; temperature 1300°C and holding time 48 h) are represented graphically in Fig. 89. As we see from Fig. 89, titanium was not deposited on the wire at 0°C or in the temperature

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range of roughly 320-470°C. In the former case (at 0°C), this was due to the extremely low vapor pressure of  $TiI_4$  and, consequently, its negligible concentration in the gaseous phase. In the latter case (320-470°C), the failure of titanium to deposit on the wire was due to the formation of  $TiI_2$ , which is not volatile enough in this temperature range. On the other hand, the maximum rates of deposition of the metal were noted at reaction-vessel temperatures of 150-200°C or in excess of 500°C (525-550°C).

Thus, the thermal-dissociation process can be advanced successfully by low-temperature or high-temperature iodination of crude titanium, working at temperatures around 200 or above 500°C, respectively. Although either of these processes — low-temperature or high-temperature — can be effected in apparatus of the same design, they differ in the mechanism of the chemical reactions that take place, since the refined metal is transported by its higher iodide in the low-temperature process and by lower iodides in the high-temperature process.

Rolsten [2] performed extremely interesting experiments in which he compared the rates of deposition of titanium from titanium iodides of various valences under conditions that practically excluded disproportionation of the lower iodides. The reaction was carried out in a quartz flask with a tungsten heater filament 20.3 cm long and 0.178 mm in diameter, which was heated to 1470°C; the rates of metal deposition on the wire from titanium tetra-, tri-, and diiodide were 0.012, 0.036, and 0.028 g/(cm·h), respectively.

The high-temperature and low-temperature variants of the iodide process yield somewhat different results. In the high-temperature process, the metal is refined of certain impurities to a greater degree than in the low-temperature process. This applies, for example, to such an impurity as iron, which is formed when the volatile iodide  $FeI_3$  reacts with iodine. This iodide is quite unstable at temperature around 500°C and, undergoing reduction by the starting titanium to the nonvolatile  $FeI_2$ , is transported to the hot wire to a much lesser degree. Transport and deposition

of silicon, whose iodides are unstable at high temperatures, and also of certain other impurities, such as chromium, manganese, nickel, and phosphorus are also reduced in the high-temperature process [17, 25]. This gives the high-temperature process a substantial advantage over the low-temperature version. In specifying temperatures for iodide method production of titanium, however, it is necessary to take account of the nature of the structural materials from which the apparatus is built (glass, quartz, metal).

Titanium tetraiodide can be used instead of elementary iodine as the iodinating reagent in refining titanium by the iodide method [26, 39].

When iodine is used, the operations of iodinating the titanium and thermal dissociation of the resulting iodide are usually combined in the same apparatus. This so-called "combined process" is the one used in most practical cases. However, when titanium tetraiodide is the iodinating agent, it is prepared in a special apparatus or in a separate part of the installation and only then introduced, without coming into contact with air, into the reaction vessel, in which the titanium is deposited on the glowing wire. Although its equipment is more complex, this so-called "separate" process using titanium tetraiodide has an important advantage over the "combined" process. In virtue of the lower activity of this iodinating agent as compared with iodine, it permits more thorough purification of the titanium of impurities present in the starting metal, and also permits intermediate purification of the titanium tetraiodide.

As is noted in the literature [10, 39], many different methods can, in principle, be used to purify the iodides of metals to be refined when the iodides are prepared in a separate operation: filtration, crystallization from solutions, distillation, sublimation, rectification, fractional condensation, zone purification, and certain other methods based on utilization of specific properties of the impurity elements. Thus, titanium tetraiodide can be purified of aluminum, whose iodide  $AlI_3$  has a boiling point close to that of  $TiI_4$ , by taking advantage of the ability of this

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element to form, on addition of KI, the compound  $KAlI_4$ , which is not volatile at dark red incandescence, while  $TiI_4$  is easily distilled off at these temperatures [27].

#### Dependence of Iodide Refining on Process Conditions

The conditions under which the iodine reacts with the starting metal must, first of all, deliver an acceptable rate of formation of the iodide, e.g., titanium tetraiodide, and the required concentration of its vapor in the reaction vessel.

It is extremely important to create conditions suitable for the transport of the new titanium tetraiodide molecules and especially for their diffusion near the glowing surface of the wire, on which the reaction



takes place.

The over-all heat effect of this reaction is 149 kcal, and its isobaric-isothermal potential  $\Delta Z_{298} = -148.8$  kcal/(mole·deg) [37]. Since, as we see from the above equation, thermal dissociation results in formation of four iodine atoms from one  $TiI_4$  molecule, an iodine partial pressure gradient develops from the wire toward the charge, making it difficult for the tetraiodide particles to diffuse. Thus the progress of the iodide process is strongly influenced by distance from the charge to be refined to the hot wire, in addition to the vapor pressure of the tetraiodide.

The temperature to which the wire is heated must provide an adequate rate of thermal dissociation of the tetraiodide with deposition of titanium on the wire and return of the iodine — the "carrier" of new portions of the refined metal — back to the process.

Runnals and Pidgeon [13] made a detailed study of the rate of deposition of metal in the iodide process as it depends on the iodine vapor pressure, the relative positions of the metal to be refined and the filament, and the temperature of the filament. Because of the high chemical activity of iodine and titanium iodides, they studied the reaction of titanium with iodine and the

rate of metal transfer to the wire in glass apparatus, collecting the iodide product in a condenser.

The authors established that the rate of metal deposition in the iodide process depends strongly on the iodine vapor pressure in the reactor space, which is determined at constant wire temperature by the temperature to which the reactor walls are heated.

As we noted earlier, the vapor pressure of  $TiI_4$  can be computed as a function of temperature by the empirical equation (4), which was submitted in [18]. According to this equation, a titanium tetraiodide vapor pressure of 0.5 mm Hg corresponds to 100°C and 5.75 mm Hg to 175°C.

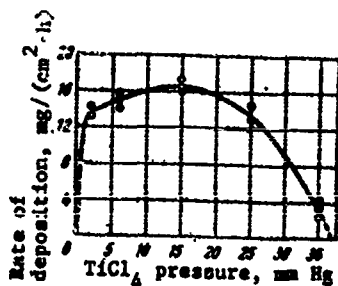


Figure 90. Influence of titanium tetraiodide pressure on rate of metal deposition (rate of metal deposition (wire temperature 1500°C)).

the rate of its thermal dissociation on the surface of the incandescent wire decreases (owing to the lower degree of dissociation of  $TiI_4$  when its vapor pressure rises), with the resulting decline in process productivity. Thus, even though the  $TiI_4$  vapor pressure rises when vessel temperature is increased above 200°C (25 mm Hg at 221°C and 35 mm Hg at 233°C), the rate of deposition of metal on the wire declines and the process comes to a virtual halt. This results from the higher rate of formation of titanium diiodide, which may react with the tetraiodide to form the involatile titanium triiodide [3]:

The influence of titanium tetraiodide vapor pressure on the rate of metal deposition is represented graphically in Fig. 90, after the authors of [13].

As the diagram shows, the rate of titanium deposition on the wire increases with increasing  $TiI_4$  vapor pressure in the vessel from 2 to 15 mm Hg, to which reaction-vessel temperatures of 146 and 204°C, respectively, correspond. On a further rise in the titanium tetraiodide vapor pressure,

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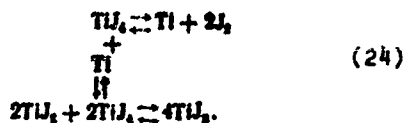


The iodide process resumes only at higher temperatures (above 500°C), when the diiodide has become volatile enough to replace titanium tetraiodide as the bearer of the metal.

As we have noted, wire temperature strongly influences the course taken by iodide refining. In order to control contamination of the rod obtained by thermal dissociation of titanium iodide, it is desirable to use a wire made from the same metal. Various reactions with titanium iodides may take place on the titanium wire, depending on the temperature to which it is adjusted [29].

At temperatures below 1100°C, a titanium wire reacts rapidly with titanium tetraiodide to form the diiodide, which, in turn, reacts with  $\text{TiI}_4$  and is converted to  $\text{TiI}_3$ . The reaction vessel contains a mixture of  $\text{TiI}_2$  and  $\text{TiI}_3$ , in which the proportions of the di- and triiodides depend on temperature. When the temperature of the titanium wire exceeds 1100°C, the titanium tetraiodide decomposes into titanium and iodine without formation of intermediate compounds.

These reactions can be represented by the equations



At titanium-wire temperatures below 1100°C, the equilibria are shifted counterclockwise; at temperatures above 1100°C, the equilibria shift clockwise, a process accompanied by deposition of titanium and evolution of free iodine.

Wire temperature was varied from 1100 to 1550°C in [13] to study its influence on metal deposition rate. The tetraiodide

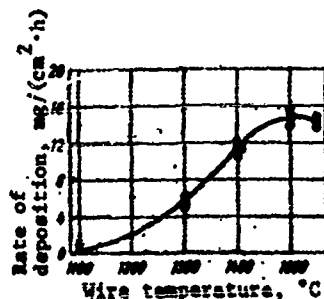


Figure 91. Influence of wire temperature on rate of titanium deposition ( $\text{TiI}_4$  pressure 6 mm Hg).

pressure was held constant in all experiments at 6 mm Hg (for which purpose the vessel was heated to 175°C). As Fig. 91 indicates, the titanium deposition rate increases as wire temperature is raised from 1100 to 1500°C. On a further increase in wire temperature (from 1500 to 1550°C), there was no increase in metal deposition rate. This is explained by the fact that the influence of the metal's volatility is perceptible at 1500°C and higher temperatures [in a vacuum at 1500°C, titanium evaporates at a rate of 12.6 mg/(cm<sup>2</sup>·h)] [30].

In view of the danger of melting of a nonuniformly heated wire and the results of Runnals and Pidgeon, which indicate that the rate of deposition of the metal on the wire from the tetraiodide is independent of temperature when the wire is heated above 1450-1500°C (since each molecule of the tetraiodide dissociates completely on contact with the wire), an effort is made to prevent wire temperature from exceeding 1400°C. Since the stability of titanium diiodide does not differ appreciably from that of titanium tetraiodide at high temperatures, it may be assumed that the wire temperature needed to ensure full dissociation of the diiodide will be close to that required to dissociate the tetraiodide.

The form in which titanium is deposited on the wire also depends on its temperature [17]. Metal produced at low temperatures has a coarse, rough surface consisting of dendritic crystalline formations. Rods produced at high temperatures have smooth surfaces and consist of large crystals with sharply bounded crystalline planes.

It was confirmed experimentally in [13] that the rate of metal deposition in the iodide process is highly sensitive to the geometrical parameters of the system and primarily to the relative positions of the metal to be refined and the filament. Process rate depends on the speeds with which the titanium iodide is moved to the filament and the elementary iodine is removed from it. Hence the distance between the hot wire and the original titanium must be as short as is permitted by design considerations. At the same time, the design of the apparatus must create uniform

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iodine vapor concentration throughout the volume of the reaction vessel, since this is necessary for uniform deposition of the metal over the length of the wire. Nonuniform deposition of the titanium produces local hot spots, and the bar melts through because of electrical-resistance variations over its length.

To prevent the bar from burning through, it is necessary to monitor wire (bar) temperature closely. When the work is done in glass apparatus, temperatures can be measured with an optical pyrometer (introducing appropriate corrections for absorption of the rays by the gaseous atmosphere and the reaction-vessel glass); metallic apparatus requires special techniques, which will be set forth below. Neither excessively high (over 1300-1500°C) nor excessively low wire temperatures may be permitted in the iodide refining of titanium, since in the latter case the deposited titanium may interact with the tetraiodide (when the reaction vessel is being operated at low temperature), and this also causes the wire to burn through.

Footnotes

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- 469 <sup>1</sup>See also patent (USA), No. 1,671,213, 1928.
- 469 <sup>2</sup>Patents (USA), No. 553,296, 1896; No. 1,019,394, 1912.
- 471 <sup>3</sup>Patent (USA), No. 3,062,615, 1962.
- 472 <sup>4</sup>See also patent (USA), No. 2,670,270, 1954.
- 474 <sup>5</sup>For the titanium diiodide disproportionation equation (11), which was proposed by Fast and other investigators [15, 17], the free energy of the reaction is determined, according to Herczog and Pidgeon [19], by the empirical formula  $\Delta G^\circ = -59400 + 3.6716T + 2.17 \cdot 10^{-5} T^2 - 72.9T$ .

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## Chapter 19

### TECHNOLOGY OF THE PROCESS

#### Iodide Refining in Glass or Quartz Apparatus

As we noted above, crude titanium can be refined by the iodide method in either a "combined" or a "separate" process. Both are discussed in the literature as conducted in glass or quartz apparatus and both will be examined below to illustrate the production-equipment side of the iodide titanium production process.

#### Graphic Not Reproducible



Figure 92. Reaction apparatus for production of iodide titanium. a) Electrode head and flask; b) perforated molybdenum shield.

The apparatus used in [25] to prepare the metal by the "combined" method is illustrated in Fig. 92 and represented schematically in Fig. 93.

Vacuum flask 11, which is 190 mm in diameter and about 890 mm high, is fitted at the top with a neck 60 mm in diameter, terminating in a fused-on electrode head 7 with four sealed-in tungsten electrodes and lead-ins 6, 8, and 9, which do not react with iodine. Tungsten filament 10, which is 0.07 mm in diameter, is attached to the electrodes; the authors used two filamentary "pins," each 610 mm long. Perforated molybdenum shield 12 (the

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"girdle") was placed inside the flask to permit uniform heightwise distribution of the crude titanium charge.

The reaction flask was heated by a furnace with a nichrome winding. The furnace heats and outgases the metal to be refined and maintains suitable temperature conditions in the flask during the initial stage of the process, when the power supplied to the heater filament is low. However, as the process advances and the electric power supplied to the wire rises, it may come to exceed the level necessary to maintain reaction-flask temperature. This requires cooling of the flask, for which purpose the furnace has a copper coil 6 mm in diameter with a row of 0.8-mm-diameter holes that provide for air cooling of the flask during the last stages of the process. A vacuum is set up in the system with mechanical forevacuum and oil diffusion pumps. The apparatus is provided with electrical equipment and instruments that permit regulation of the current supply from 0.5 to 300 A.

The authors of [25] produced the purified metal by the following procedure.

The crude metal is placed in the annular space between the wall of the glass vessel (flask) and the perforated molybdenum screen; a full load of titanium (in the form of fragments ranging in size from 6 to 13 mm) weighs about 5 kg. Then the electrode head with the tungsten filament suspended from it is inserted into the flask and sealed in position; to position it properly at the bottom of the flask (Fig. 93), the filament is connected via quartz insulators 14 to special tungsten weight 15. The suspended system is secured to molybdenum platform 13. To test the joints, a vacuum is set up in the flask and it is checked for vacuum-tightness. Then, as is shown in Fig. 93, the flask is sealed to vacuum system 3 and the production process is carried out in the

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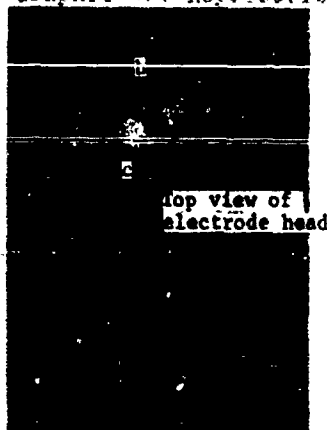


Figure 93. Schematic drawing of reaction flask used to produce iodide titanium.

assembled unit.

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Figure 94. Titanium "pin" produced on thermal dissociation of the iodide.

The entire system is evacuated and the flask is heated to 525°C, at which temperature it is held for 4 hours. After heating and outgassing of the metal, the flask is cooled to room temperature and helium is admitted to it through the liquid-air trap 5. Then 100-300 g of iodine is introduced through neck 1 of receiver A into flask 4, with simultaneous back-flushing with helium. The end open for the iodine is sealed off at point 2, the iodine is cooled, and a vacuum of the order of  $10^{-4}$  mm Hg is set up in the system, at which point the receiver with the iodine is disconnected from the vacuum system by sealing the tube at point B. The iodine is then distilled over into the reaction flask with gentle warming, and the tube is resealed at point C. During iodide refining of the titanium, the reaction flask is heated in an electric furnace throughout the remainder of the process to 175-200 or 500-550°C, depending on whether the process is to be run at low or high temperature. Filament temperature, which can be regulated by varying the amperage of the current passed through it, is held in the 1300-1400°C range. At a final filament current of 250 A, the rods obtained are about 8.5 mm in diameter. Figure 94 shows a typical titanium "pin."

The process carried out in this unit yields two "pins" of the metal with a total weight of 600 g; the cycle takes about 30 hours at a reaction-flask temperature of 175°C. This study reports that iodide refining of 98.6% titanium increases the content of the principal element to 99.8-99.9%. Titanium prepared by the iodide method is highly plastic. For example, it is reported [40] that the ultimate strength of this metal is about 21 kgf/mm<sup>2</sup> at a

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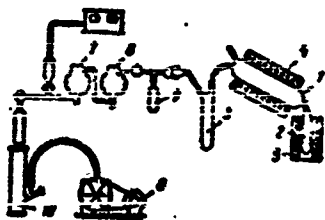


Figure 95 Diagram of apparatus for iodination of titanium.

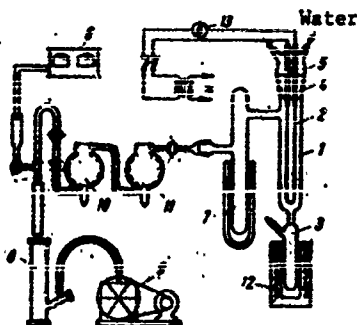


Figure 96. Diagram of installation for thermal dissociation of titanium tetraiodide.

diamond-pyramid hardness of 60. These high plastic properties result chiefly from the sharp decrease in the metal's content of hardening impurities, and gases in particular — oxygen and nitrogen. However, as is evident from the chemical analyses to be given below, the method is rather ineffective in the removal of iron, aluminum, silicon, carbon, and certain other impurities that form volatile iodides, some of which are transferred into the final metal.

Figure 95 shows a diagram of the apparatus used in [39] for the separate version of the process. For iodination, the starting titanium was placed in quartz reaction flask 1, and the iodine in flask 2 and heated by furnaces 4 and 5, respectively. In the optimum process that was established, the iodine was heated to 80-110°C and the titanium to 230°C; the residual pressure in the system, which was evacuated with mechanical vacuum and diffusion pumps 6 and 10 (which were protected from iodine and tetraiodide vapor by liquid-nitrogen traps 7 and 8), was around  $3-4 \cdot 10^{-3}$  mm Hg. The titanium tetraiodide formed in reaction flask 1 was simultaneously distilled and collected in receivers 3 and 9. The authors of [39] report that their product corresponded almost exactly to the theoretical composition of titanium tetraiodide.

The titanium tetraiodide was thermally dissociated (Fig. 96) in a quartz reactor 1 on molybdenum or titanium wire 2 after the wire had been heated by electric current to 1400-1500°C; the wire

was secured to electrodes 4, which were sealed into water-cooled molybdenum-glass head 5. The current in the wire was measured with ammeter 13, and heating of the wire was monitored with an optical pyrometer. The system was evacuated by mechanical and diffusion-type vacuum pumps 8 and 9, which were protected from vaporized dissociation products by condenser 7 and liquid-nitrogen traps 10 and 11.

Before the process was started, the system was thoroughly outgassed, after which flask 3 with the  $TiI_4$  was sealed to the apparatus; on heating of this flask by furnace 12 to temperatures near the melting point of  $TiI_4$ , the latter evaporated and entered reactor 1. The process was initiated and conducted at a residual pressure  $<1 \cdot 10^{-4}$  mm Hg, which was measured by vacuum gauge 6.

The authors of the study report that the final metal has an impurity content on the level of ordinary iodide titanium and, in some cases, considerably below that level.

According to the technical specifications of the American Society for Testing of Materials [28], the impurity contents in iodide titanium may not exceed (%): 0.02 Fe, 0.02 Si, 0.03 Al, 0.04 Mn, 0.03 C, 0.01  $N_2$ , 0.01  $O_2$ , and 0.01 other impurities.

According to [2], the impurity contents in iodide titanium were actually (%): 0.01 Fe, 0.001 Si, 0.05 Al,  $<0.01$  Mn,  $<0.01$  V,  $<0.01$  Sn, 0.005 Cu, 0.01 Zr,  $<0.002$  Cr,  $<0.005$  Mo,  $<0.01$  Ni,  $<0.005$  Pb, 0.005 Mg, 0.006  $N_2$ , 0.005  $H_2$ ,  $\sim 0.01$   $O_2$ .

#### Iodide Refining in Metallic Apparatus

Use of glass apparatus similar to that described above is not suitable for large-scale production (as a convention, we shall refer to "industrial" production) of the metal by the iodide process. Such equipment is incapable of producing substantial amounts of refined metal in each production cycle, since the heavy currents required to produce large-diameter bars cannot be passed through the bars in glass reactors owing to the strong thermal radiation. Glass equipment is further unsuited for use under industrial conditions because of its brittleness, sensitivity to thermal shock, and unfitness for service at high temperatures.

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These deficiencies can be eliminated by using metal instead of glass equipment. Unlike glass apparatus, these installations can be built on a larger scale without permanent joints, since packings made from appropriate metallic or thermostable polymer materials or vacuum rubber can be used.

However, the use of metallic apparatus for the preparation of titanium and other high-melting metals by the iodide process was rendered extremely difficult by the restricted choice of materials resistant to the aggressive action of iodine and iodide vapors at elevated temperatures. All ordinary structural materials are unsuitable for this purpose, since they corrode under the process conditions and contaminate the metal product. Although Van Arkel and de Boer made reference in their 1928 patent<sup>(1)</sup> to the utility of chrome steel for this purpose, the literature has offered no data supporting the possibility of practical use of apparatus made from this material in the iodide process. Information on materials whose anticorrosion properties render them suitable for the fabrication of iodide-process equipment was long absent from the literature. Various metals and alloys were tested in an atmosphere of iodine vapor at a pressure of 400 mm Hg and temperatures of 300 and 450°C [31]. Below we present the results of tests to determine the corrosion rates of various materials at these temperatures in an iodine-vapor atmosphere, in units of  $10^{-6}$  cm/day:

|                     | 300°C | 450°C |
|---------------------|-------|-------|
| Platinum            | 0     | 1.5   |
| Tungsten            | 0     | 2.2   |
| Gold                | 0     | 6.5   |
| Molybdenum          | 0.9   | 9.0   |
| Tantalum            | 1.2   | 241   |
| Hastelloy B**       | 12.1  | 127   |
| Hastelloy C**       | 15.5  | —     |
| Inconel             | 29.2  | 148   |
| Nickel              | 75.2  | 332   |
| Stainless steel 310 | —     | 487   |
| Stainless steel 316 | —     | 563   |

Footnote (1) is on page 507.

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|  |                   |       |
|--|-------------------|-------|
|  | 300°C             | 450°C |
| Stainless steel 347  | —                 | 569   |
| Monel metal  | 154.0             | 713   |
| Silver   | Reacts completely |       |
| **Nickel-molybdenum-based alloys [32]. Composition of<br>Hastelloy B, in %: 60-65 Ni, 25-35 Mo, 5 Fe, 0-0.5 Mn.<br>Composition of Hastelloy C, in %: 50-58 Ni, 16-18 Mo,<br>4-5.7 Fe, 15.5-17.5 Cr, 1 Mn, 1 Si, 3.75-4.75 W. |                   |       |

On the basis of the completed corrosion tests, Hastelloy B and Inconel were recommended in [31] as structural materials for the fabrication of iodide-process reaction equipment. Molybdenum is recommended for various internal components of the apparatus that are subject to unusually severe corrosion conditions.

Other investigators [33] tested the corrosion stability of nickel and nickel-based alloys under the conditions of the real iodide process (at a temperature of the order of 350°C). These studies indicated that among the materials tested, alloy Kh20N80, which contains 20% Cr and 80% Ni, was found to be comparatively more stable. The authors report that when iodide titanium was prepared in a laboratory reactor made from this alloy, corrosion resistance was quite satisfactory, and this enabled them to specify nichrome as a structural material for a semiindustrial unit. It was established as a result of laboratory tests on a number of packing materials — vacuum rubber, pure aluminum, Teflon (Ftoroplast), annealed copper, and then nickel-plated wire — that the first two materials are suitable, and vacuum rubber, cooled by water supplied through grooves in the reactor flange, was selected for the semiindustrial apparatus.

Until quite recently, the literature offered practically no data on the preparation of iodide titanium in metallic apparatus [3]. However, some data were published on the use of such apparatus for the preparation of iodide zirconium [31], and they were received with just as much interest for their bearing on iodide titanium and put to use by researchers engaged in work on the production of the latter metal.

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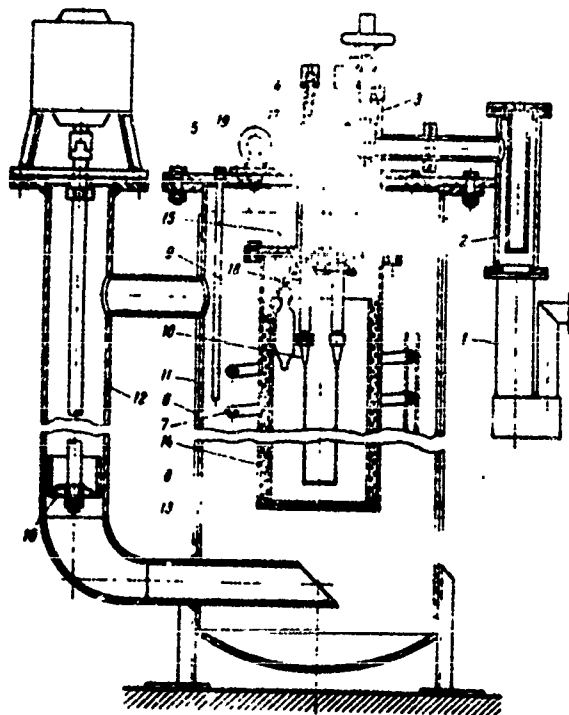


Figure 97. Metallic apparatus for the iodide process. 1) Hard-vacuum pump; 2) freeze-out unit; 3) valve; 4) copper electrode; 5) thermocouple; 6) tank with temperature-stabilized liquid; 7) cooling coil; 8) molybdenum shield; 9) zirconium tetraiodide bottle; 10) molybdenum electrode pole piece; 11) ribbon-type heaters; 12) circulation tube; 13) unit made from Hastelloy B alloy; 14) zirconium sponge; 15) ceramic liners; 16) stirrer with case; 17) packing ring; 18) zirconium wire for attachment of bottle; 19) liquid level.

Figure 97 shows an experimental unit by Westinghouse for production of iodide zirconium. A distinctive design feature of this apparatus is that the entire reaction flask, including the cover, is immersed in a liquid constant-temperature bath to stabilize its temperature. The apparatus is made from Hastelloy B and is 305 mm in diameter and 1220 mm high. The molybdenum screen that separates the sponge space is 267 mm in diameter and positioned concentrically in the reactor.

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The 25.4-mm-diameter electrodes consist of two sections. The lower section, which is subject to exposure to iodine and iodide vapor, is made of molybdenum, while the upper section, which is attached to it and extends through the cover of the unit, is made from copper. Water-cooling passages are drilled axially through the copper parts of the electrodes. The electrodes are insulated from the cover of the apparatus by nonporous ceramic bushings (made from aluminum oxide or zirconium dioxide). The cover packing is of gold (wire 0.89 mm in diameter). The authors of the design justify the use of this packing material by the high corrosion stability of gold, which is fully retained even after remelting and drawing of wire suitable for reuse. Thus, they find the use of gold as a packing material economically expedient in spite of its high cost.

It is especially difficult to design valves for iodide equipment. Conventional packed valves are unsuitable under the conditions of the iodide process. The same applies to unpacked bellows-type vacuum valves, which are unsuitable because of the corrosion and cracking caused by condensation of the solid on the turns of the bellows. Diaphragm-type valves are of little help, since the clearance between the seat and plunger is too small in the open position in valves of suitable size, and this prevents quick pumping of the apparatus [31].

As we see from Fig. 97, the valve used in this unit is of special design and incorporates a stationary water-cooled rod with a packing ring. The plunger is carefully polished and bears against an acute-angle taper machined out of the valve casing.

As we noted above, corrosion tests run on various metallic materials established that, in addition to Hastelloy B, the alloy Inconel is also suitable for building such equipment. The firm Foote Mineral manufactures apparatus made from this material for industrial production of iodide zirconium. The firm has installed a large number of Inconel units 229 mm in diameter and 610 mm high in one of its shops; they produce 2.7 kg of metal per cycle (32 hours) [34]. Two series-connected heaters in the form of pins 2.5 mm in diameter with a single-arm length of 483 mm are

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suspended in the head of each unit.

The units are held at temperature (about 340°C) during the process by means of small salt baths with automatic air cooling.

In contrast to Foote Mineral, the firm Westinghouse considers it advantageous to use equipment with substantially higher (by a factor of 10 to 20) per-cycle productivity in industrial production of iodide zirconium. Figure 98 shows a schematic sectional drawing of this unit. It is also thermostated by means of a salt bath to maintain process temperature. The bath is heated by internal heaters, and heat is withdrawn by water injected into a shell surrounding the bath. The apparatus is 61 cm in diameter and 1.7 m high and uses an initial heater 2.4 mm in diameter and 15.2 m long. This heater is bent to form a series of six "pins" and suspended vertically between two round plates secured to the unit's cover. The cover and case of the unit are sealed with a gold packing 0.9 mm in diameter. The electrode design is similar to that described earlier. At an average metal deposition rate of about 0.4 kg/hour, the unit delivers 53 kg of refined zirconium in a cycle (in which the power dissipated by the bar range 75 kW). Modernization of the Westinghouse unit raised its per-cycle output and more than doubled the rate of metal deposition per unit heater length [31]. It was improved by placing a layer of cooled sponge inside the cylinder formed by the heaters and modifying the salt baths to provide appropriate cooling (Fig. 99).

The modernized unit was capable of growing substantially larger bars of the metal as a result of the increased heat-dissipation surface obtained by introduction of a central cooling pipe.

Until very recently, very little information was published on the production of iodide titanium in metallic equipment.

Gonser published a report [35] on the preparation of iodide titanium in laboratory-scale metallic apparatus. The unit used for this purpose was 114 mm in diameter and 762 mm long and could produce titanium bars of satisfactory quality in the form of rods 610 mm long, up to 16 mm in diameter, and weighing from 700 to 750 g. The cycle time in his experiments ranged from 30 to 48

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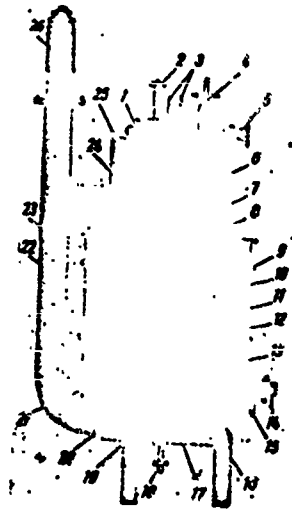


Figure 98. Westinghouse metal equipment. 1) Iodine; 2) iodine tank valve; 3) electrodes; 4) main vacuum valve; 5) safety valve; 6) Hastelloy support plate; 7) zirconium sponge; 8) molybdenum shield; 9) water nozzles; 10) initial zirconium wire; 11) cooling jacket; 12) Hastelloy tank; 13) ceramic insulators; 14) vapor exit; 15) condensate drain; 16) Hastelloy support plate; 17) molybdenum heat shield; 18) fused-salt drain; 19) weight; 20) guides; 21) molybdenum-wire tie-down; 22) draft circulation pipe; 23) flexible joint; 24) fused salt; 25) thermocouple sleeve; 26) mixer electric motor.

trial-scale production of iodide titanium in metallic equipment in the USA. The units were said to have a per-cycle output of 15 kg, in the form of titanium bars about 30 mm in diameter. However,

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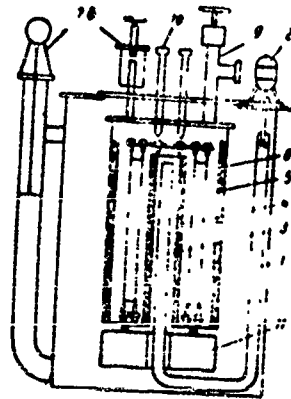


Figure 99. Modernized Westinghouse metal apparatus (schematic sectional drawing). 1) Circulation tube; 2) electric motor for circulation pump; 3) internal cooling tube; 4) central layer of sponge; 5) multi-loop heater; 6) vaporizer; 7) main circulation pump; 8) outer sponge layer; 9) valve; 10) electrodes; 11) weight.

hours. Electric power consumption was around 90 kW·h per kilogram of metal.

In submitting the results of his production-engineering experiments, the author unfortunately gives no information on the material of which the reaction apparatus was built.

Later reports [36] made reference to the routine industrial-scale production of iodide titanium in metallic equipment in the USA. The units were said to have a per-cycle output of 15 kg, in the form of titanium bars about 30 mm in diameter. However,

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no information is given on the structural materials used to build the equipment.

Later publications gave rather detailed information on the design and process conditions of all-metal industrial-type apparatus for the production of iodide titanium with a design cycle output of 24 kg, or 10 kg of metal per day [33, 37].

The reactor, a schematic drawing of which appears in Fig. 100 [37], is a cylindrical vessel made from Kh20N80 alloy, has a flush cover, and is designed for work in a vacuum. The charge to be refined (crude titanium) is placed in the space formed between the reactor inner walls and a cylinder of molybdenum screening stretched on a molybdenum-rod framework. The titanium filament (3-4 mm thick) is

wound on a special fixture with tungsten-wire tensioners secured in steatite insulators. The total design length of filament is about 11 meters. A vacuum-rubber gasket cooled by water flowing through a groove is used to seal the cover to the unit.

The amount of iodine required for the process is introduced into the unit in a sealed glass ampule, which is placed in a device inside its cover (the ampule holder). After assembly, the gasses are pumped out of the unit and the charge of crude titanium by series-connected forevacuum (VN-1) and oil-diffusion (N-5) pumps and the retort is heated. When a residual pressure of the order of  $10^{-4}$ - $10^{-5}$  mm Hg has been reached in the apparatus, pumping is stopped, the vacuum slidegate is closed, the reactor is disconnected from the vacuum system, and the iodine is released into the reactor, which is now at 200°C. This is done by investing the ampule-holder cylinder in a heating coil and simultaneously removing the sealoff from the ampule (by overheating it with

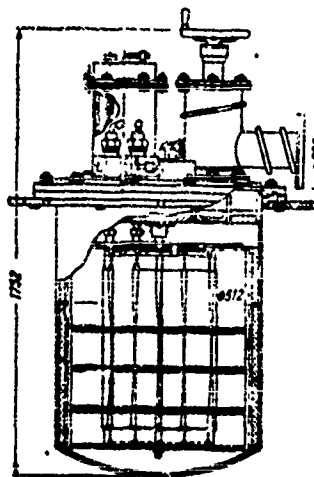


Figure 100. Industrial-type metallic unit for production of iodide titanium.

electric current or breaking it off with a special prod). After admission of iodine into the reactor, a certain amount of time is allowed for formation of the necessary amount of titanium tetraiodide, current is switched into the wire, and the process of depositing the iodide titanium is started. An air-washed constant-temperature bath was tested for removal of heat from the reactor walls. However, it was found impossible to establish uniform temperature on the surface of the reactor and vary it in accordance with the intended schedule by regulating the stream of air fed into the thermostat tubing. The unit was subsequently thermostated with boiling water, since the same authors had established in laboratory experiments that iodide titanium is deposited at an acceptable rate even when the reactor walls are at 100°C. This thermostating principle ensures uniform temperature over the entire surface of the reactor, is easily capable of removing the heat liberated in the process, and stabilizes the process by minimizing the rate of diiodide formation. The steam formed as a result of heat offtake was diverted to a boiler condenser, from which the condensate was returned to the thermostat tank.

The electrical equipment of the installation was capable of delivering currents up to 2000 A into the wire with smooth regulation of the voltage from 220 to 20 V.

As we noted above, when the iodide process is carried out in metallic apparatus and (in contrast to glass apparatus) it is impossible to monitor heating of the wire visually, holding the wire at constant temperature becomes a rather complex task, since its diameter increases progressively and its resistance drops as titanium builds up.

To ensure constancy of wire temperature, it is necessary to regulate the voltage and current as functions of its diameter.

Since the  $TiI_4$  vapor pressure in the reactor remains constant during the process, and the heat losses from the wire through the electrodes are insignificant, it can be assumed that practically all of the electric power supplied is used to compensate for the loss of the heat radiated from the wire (bar) surface. As the

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titanium grows, the power supplied to the bar must be increased systematically to cover the heat losses, which increase as bar diameter increases. Thus, the electric power being supplied to the bar at any given part in the process must be equal to the power  $W$  radiated by its incandescent surface:

$$W = \omega S = I^2 R = \frac{E^2}{R}, \quad (25)$$

where  $\omega$  is the emittance of the titanium,  $S$  is the surface area of the bar,  $I$  and  $E$  are the current and voltage applied to the bar, and  $R$  is the resistance of the bar.

Substituting values of  $S$  and  $R$ , expressed in terms of the bar's diameter and length, into this equation together with the bar's resistivity  $\rho$ , we obtain

$$\omega \pi D L = I^2 \frac{\rho l}{\pi D^3}. \quad (26)$$

Thus, in order to determine the heat losses and, consequently, the amount of electric power to be supplied, we need to know only the emittance and resistivity of titanium at the temperature to which the titanium bar is heated. Thus, for example, these parameters are  $19.55 \text{ W/cm}^2$  and  $227 \text{ } \Omega \cdot \text{mm}^2/\text{m} \cdot 10^{-6}$  at  $1300^\circ\text{C}$  [33, 37].

Rearranging the last equation, which links the voltage and current with the geometrical dimensions of the incandescent bar, we obtain the condition under which its temperature will be held constant [31, 33, 37]:

$$IE^3 = K, \quad (27)$$

where  $K$  is a constant.

Having determined the voltages and currents for various grown-bar diameters and plotted the  $I = f(E)$  curve (the volt-ampere characteristic of the

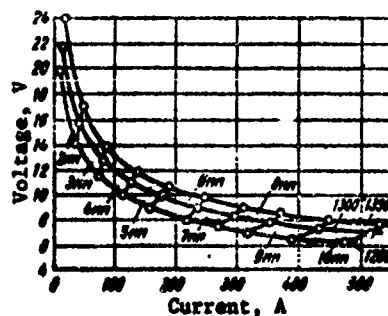


Figure 101. Volt-ampere characteristics of titanium deposition at various filament (bar) temperatures, constructed from experimentally obtained data.

process), we can regulate the temperature in the hermetically sealed metallic apparatus in accordance with this curve.

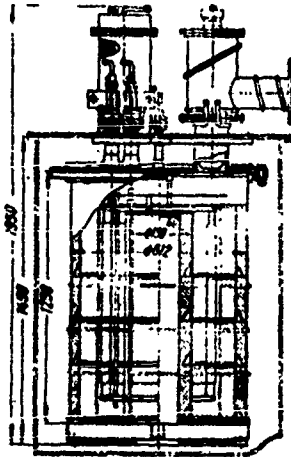


Figure 102. Metallic apparatus of industrial type with double shield.

Volt-ampere characteristics plotted by the authors of [37] for various titanium-deposition temperatures (1250-1350°C) appear in Fig. 101. The electrical parameters of the iodide-titanium production process were regulated automatically with a special device in accordance with this diagram.

It was established in experiments conducted in the industrial-type apparatus described (Fig. 100) that the metal was deposited nonuniformly on the wire, which was not centered in the cross section of the resulting bar. A thicker layer of metal settled on the side of the wire facing the charge, since the rate of the process increased with decreasing distance be-

tween them.

For this reason, the reactor design was modified by placing the crude metal on both sides of the wire, at approximately equal distances (Fig. 102); this ensured not only uniform deposition of the metal, but also a substantial increase in the rate of the process.

The authors of [33] deposited bars of iodide titanium 18-19 mm in diameter in the units described above, obtaining 10-12 kg per cycle. The metal bars were highly plastic as a result of a sharp decrease in their gaseous-impurity contents, and wires, thin ribbons, and thin-walled tubes were pressworked cold from them with reduction ratios up to 99.5-99.8% (without intermediate annealing).

### Prospects for Development of the Iodide Process

The principal disadvantage of the iodide method is the comparatively high cost of the metal produced, which results from the high cost of the starting materials and the high electric power consumption and low productivity of the process, which is intermittent (cyclical) in nature.

The cost of the initial products can be reduced substantially if the sponge is replaced by other, cheaper titanium-containing materials and provision is made for complete regeneration of the iodine. One possible approach to solution of this problem might be a method that has been proposed for preliminary preparation of titanium tetraiodide from a cheap titanium-aluminum alloy [27]. An increase in process productivity might then be expected from passing a continuous stream of tetraiodide vapor over the hot wire, since the dependence of titanium deposition rate on the rates of iodide and titanium iodide diffusion would be eliminated.

The titanium-aluminum alloy used as the starting material in production of titanium tetraiodide was produced by aluminothermic reduction of technical titanium dioxide; it contained about 70% Ti, 11% Al, 1% Fe, 1% Si, and up to 17% oxides. The principle of the method, which was described in detail by the authors of [27], is based on the fact that when this alloy is treated with elementary iodine dissolved in carbon disulfide, its principal components form iodides in the reactions



The iodides of titanium and aluminum dissolve quantitatively in carbon disulfide (on boiling for 1 hour in the absence of moisture); after this, the solution is decanted off the solid residue and the carbon disulfide is driven out. The resulting mixture of titanium and aluminum iodide crystals is then heated in a current of dry helium with potassium iodide, whereupon the potassium and aluminum iodides react with one another, forming the nonvolatile compound  $\text{KAlI}_4$  and the titanium tetraiodide is distilled off and condensed. Titanium tetraiodide prepared by this method contains

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less than 0.01% of impurity aluminum and can be used to produce the iodide metal.

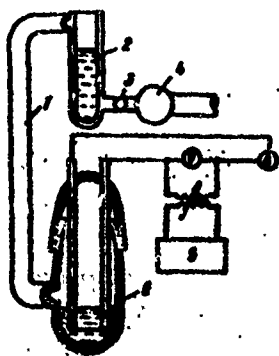
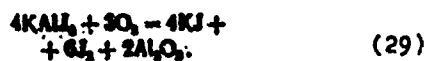


Figure 103. Apparatus for deposition of titanium from boiling film. 1) Condenser; 2) vapor trap; 3) valve; 4) vacuum pump; 5) power supply; 6) reaction flask.

The method has an advantage in the possibility of extraction of the most valuable component — the iodine (elementary and in the form of potassium iodide) — from the reaction products; this is accomplished by heating the potassium iodoaluminate to a red glow and passing dry air through it:



This method, which is based on use of an inexpensive raw material to produce iodide titanium and permits practically complete (98%, according to the authors) regeneration of the iodine, can improve the economy figures

of the iodide process substantially.

Interest attaches to the so-called boiling-film method of titanium deposition, which was tested by Petersen and Bromley on a laboratory scale [31], as a means of raising the productivity of the process and reducing the amount of electricity used. This method, which was realized in the apparatus shown schematically in Fig. 103, consists in depositing the titanium directly from liquid  $TiI_4$  by forming a boiling film around a wire heated to 1600-1740°C (i.e., to a temperature near the melting point of titanium).

The originators of the method obtained titanium-deposition rates from 1000 to 10,000 mg/(cm<sup>2</sup>·h) at an electric power consumption of 4.4 to 44 kW·h per kilogram of metal, i.e., a substantial improvement over the conventional thermal dissociation of titanium tetraiodide, for which, for example, Runnals and Pidgeon [13] recorded metal deposition rates of 10-100 mg/(cm<sup>2</sup>·h) and electric power consumptions from 88 to 158 kW·h.

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After solution of certain problems related to material selection and control of the process, this method may form a basis for a continuous or semicontinuous process.

There have also been several other proposals oriented toward development of a continuous iodide process. They include, for example, the suggestion that the iodides be decomposed in an electric arc struck between an ingot of the metal and a hollow electrode through which iodide vapor is passed [31]. Dissociation of the iodide produces the metal in the molten state, the ingot is agitated continuously as it grows, and the iodine and excess iodide are to be pumped out and condensed.

However, implementation of any of these proposals will require that major difficulties be overcome and much research be done to confirm their feasibility and establish their technical-economy indicators.

In addition to the iodide method, the subhalide method is of interest for the refinement of technical titanium; it is based on purification of the metal by disproportionation of its lower halides (for example, subchlorides, subbromides), and its development has been given a great deal of attention in Great Britain by the Palmer [transliterated from Russian] Research Institute [26].

Rammamurthy [24] made a thermodynamic analysis of certain disproportionation reactions of lower titanium halides. The free-energy changes that he computed for these reactions at 500°K are given below:

| Reaction  | $\Delta Z^\circ$ , kcal |
|---|-------------------------|
| $2 TiCl_3 \rightleftharpoons TiCl_4 + TiCl_2$ . . . . . | 24.2                    |
| $2 TiCl_2 \rightleftharpoons Ti + TiCl_4$ . . . . .     | 26.2                    |
| $2 TiBr_3 \rightleftharpoons TiBr_4 + TiBr_2$ . . . . . | 12.5                    |
| $2 TiBr_2 \rightleftharpoons Ti + TiBr_4$ . . . . .     | 22.5                    |
| $2 TiI_3 \rightleftharpoons TiI_4 + TiI_2$ . . . . .    | -4.0                    |
| $2 TiI_2 \rightleftharpoons Ti + TiI_4$ . . . . .       | 16.5                    |

\*At 1000°K,  $\Delta Z^\circ = 2.7$  kcal.  
 \*\*At 1000°K,  $\Delta Z^\circ = 13.7$  kcal.

The thermodynamic foundations of the disproportionation reactions of titanium lower halides and the subchlorides in particular were

subsequently studied by a number of investigators and are illuminated in the specialized literature [41].

Referring to the example of the free-energy changes of titanium subchlorides at various temperatures, we see that Ramnamurthy's data indicate the feasibility of a process in which the titanium tetrahalide is reduced by crude titanium to the dihalide at low temperatures, while at higher temperatures the dihalide will decompose, releasing metallic titanium.

It is this principle that forms the basis for a process proposed by the Fal'ner Institute for production of highly purified titanium. According to its authors, the lower titanium chlorides or bromides, and especially the dihalides, can be prepared easily and in high yields by treating the crude metal with tetrahalide vapor ( $TiCl_4$ ,  $TiBr_4$ ). This substantially eliminates most of the impurities usually present in the crude metal that admit with difficulty or not at all to chlorination (bromination) by titanium tetrahalides and produces titanium subhalides (subchlorides, subbromides) that are practically free of these impurities.

At ordinary temperatures, the lower chlorides and bromides of titanium have moderate vapor pressures. Thus the metal to be refined interacts with its tetrahalides at moderately elevated temperatures, at which the vapor pressures of the resulting subhalides are quite high and ensure their removal from the reaction zone.

In this process, titanium tetrachloride or tetrabromide vapor is passed at these temperatures and in an inert atmosphere (or vacuum) over the crude metal to be refined to produce the corresponding lower titanium halides in the form of vapors that are trapped in the cooled zone of the apparatus — a condenser. The condensate is then heated and the disproportionation reaction used to obtain pure secondary metallic titanium and the tetrahalide, which is condensed in the cold zone and returned to the process for halogenation of crude metal.

Crude metal can be refined in a continuous technological flow in a system consisting of two units that are heated and cooled by

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turns after connecting and disconnecting them, respectively, from the  $TiCl_4$  ( $TiBr_4$ ) current [26]. A titanium-refining process based on disproportionation of its lower halides (chlorides, bromides) was subsequently also patented in the USA.<sup>(2)</sup> However, it must be remembered that metal produced by disproportionation of titanium subchlorides or subbromides has a finely dispersed structure, and that special measures are required to eliminate oxidation when it is extracted from the apparatus. The subchloride process has an advantage for practical use over the subbromide process because of the large-scale industrial production of titanium tetrachloride and its relatively low cost. This same circumstance (the availability of an industrial technology for chlorination of titanium-containing raw materials) also gives the subchloride refining process an advantage over the iodide method, which uses the comparatively less plentiful and more expensive iodine. Yet another advantage of the subchloride method is the fact that, unlike the iodide method, not one but both stages of the process are refining, i.e., both chlorination and disproportionation, in which the metal is purified of miscellaneous chloride impurities ( $AlCl_3$ ,  $FeCl_2$ ) that settle on the condenser together with the titanium subchlorides.

The purity of titanium produced by the iodide and subchloride processes can be improved by zone melting. It has been reported that the metallic-impurity content in the titanium is greatly reduced by zone refining [42]. The authors of another paper [43], who investigated induction zone remelting of iodide titanium and certain other high-melting metals, established that under appropriate conditions (current frequency 250 kHz, bar diameter 11 mm, speed 2 mm/min, pass length 85 mm, 8 passes), the contents of iron, chromium, manganese, and silicon impurities in the refined titanium can be reduced by a factor of 10, and that of aluminum by a factor of 100.

The recent literature offers information on further progress made in the zone refining of titanium. Thus, it is reported [44, 45] that the firm Materials Research Corporation in the USA is producing ultrapure titanium with a 99.9999% content of the

Footnote (2) is on page 507.

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principal element by electron-beam noncrucible zone remelting of iodide metal. This metal, which is produced in the form of rods, wires, or foils, is substantially more plastic than titanium produced by thermal dissociation of its iodides. Thus, titanium rods produced by zone purification (6.35 mm in diameter) are so plastic that wires 0.25 mm in diameter can be drawn from them without intermediate annealing.

The ultrapure titanium is expensive (rods 0.6 cm in diameter cost \$40 per 2.5 cm and wires 0.5 mm in diameter \$2.50 per 30.5 cm), and its uses are therefore severely limited — for example, in electronic devices and other critical fields of application. Thin films produced by vaporization of ultrapure titanium in a hard vacuum are extremely valuable to the electronics industry.

Iodide titanium purified by electron-beam noncrucible zone remelting is used as a starting material in the preparation of single crystals of this metal [38, 46]. Titanium single crystals are grown by slow displacement of the molten zone along a solid ingot in such a way that crystallization centers form in the low-temperature  $\alpha$ -phase and single-crystal growth begins from them in the high-temperature  $\beta$ -phase.

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<sup>1</sup>Patent (USA), No. 1,671,213, 1928.

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<sup>2</sup>Patent (USA), Nos. 3,001,865, 3,001,866, 3,001,867,  
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Part VI

SMELTING OF TITANIUM, REFINING OF CERTIFIED SCRAP,  
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Chapter 20

SMEETING INGOTS FROM TITANIUM AND  
TITANIUM-BASE ALLOYS

Many Soviet and foreign studies have been devoted to the smelting of titanium and titanium-based alloy ingots. A large amount of factual material on the technology of smelting and furnace designs for this purpose is available in the monographs [1, 2, 143], which were written by teams of Soviet authors.

Development of a technology for smelting titanium required that the following series of obstacles be surmounted: at high temperatures, and to an even greater degree in liquid form, titanium reacts vigorously with all refractory materials, including the oxides usually used in refractories, with the result that it becomes contaminated by oxygen and loses plasticity. Smelting of titanium in graphite crucibles results in its contamination by carbon, which also lowers the mechanical characteristics of the metal appreciably.

A method in which titanium is smelted in an electric-arc furnace with a water-cooled copper crystallizer has been found most suitable. The electric arc burns between an electrode made from a high-melting material (nonconsumable electrode) or from metal to be remelted (consumable electrode) and a molten pool of this metal. The metal next to the cold walls of the crystallizer chills very quickly and melting actually takes place in a titanium

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lining. Since the lining does not adhere to the crystallizer walls, a moving bottom can be used, so that the ingot can be extracted from the crystallizer during the smelting process. A fixed-bottom crystallizer can also be used (this is the most commonly encountered design), but then the height of the crystallizer and the entire design must be much greater, and this makes the unit itself and the shop building more expensive.

In practice, tungsten coated with thorium to increase its electron emission and graphite impregnated with titanium to reduce carbonization of the smelted ingot have been used as nonconsumable electrodes in titanium smelting. Smelting has been carried out in an argon or helium atmosphere or a mixture of these gases under a partial vacuum (about 200-250 mm Hg). The electrode was positioned eccentrically in the furnace to obtain uniform heating of the molten-pool surface. As it was turned, the electric arc described a circle and heated the entire surface of the liquid metal pool. Titanium ingots weighing up to 1000 kg have been smelted out in arc furnaces with nonconsumable graphite electrodes [3].

Arc furnaces in which high-melting metals are smelted operate on direct current, with the ingot usually serving as the anode, since more energy is released at the anode than at the cathode (about two-thirds). This current supply to the furnace is referred to as the forward polarity. Figure 104 presents a diagram of an arc furnace with nonconsumable electrode for smelting titanium ingots.

Industrial use of arc furnaces of this design for smelting titanium was short-lived, since they have the following disadvantages:

a) contamination of the ingot by inclusions of material from the nonconsumable electrode. When smelting was done with a tungsten electrode in inert gases, splashing of the metal struck the electrode and eroded it. During subsequent pressworking of the ingot, the inclusions of the Ti-W alloy broke up, forming various types of defects. Use of graphite electrodes improved the situation somewhat in this respect;

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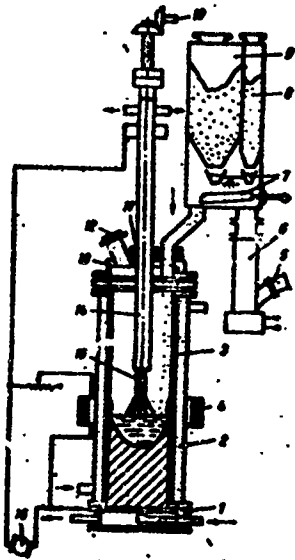


Figure 104. Diagram showing construction of vacuum-arc furnace with nonconsumable electrode. 1) Water-cooled copper bottom; 2) jacket made from nonmagnetic material for cooling of crystallizer; 3) copper crystallizer; 4) solenoid; 5) flange for attachment of forevacuum pump; 6) booster pump; 7) automatic weighing batcher; 8) hopper for alloying additives; 9) hopper for sponge; 10) electrode feed mechanism; 11) sliding vacuum packing; 12) inspection window; 13) cover; 14) water-cooled copper electrode holder; 15) graphite electrode; 16) dc generator.

electrodes made from the charge to be smelted and electromagnetic

b) premature chilling of the ingot, which produced an irregular surface; when the ingot was roughed down, as much as 25% of the metal was lost in the shavings;

c) the molten pool is shallow and not well agitated, with the result that the ingot is strongly inhomogeneous over its cross section and height;

d) feeder performance did not ensure delivery of the alloying components in the proper proportions, and this also tended to make the ingots nonuniform in chemical composition;

e) evolution of gases during smelting of the metal causes it to spatter. On striking the crystallizer walls, these splashes solidify and form a "crown," which interferes with rotation of the electrode (if the furnace design provides for rotation) and produces short circuits. As a result, it is necessary to load the charge into the furnace slowly [1, 3, 4].

Another reason for slow melting of the charge is the fact that about 1/3 of the energy is released at the nonconsumable electrode, an amount that increases as the residual pressure declines [5].

The smelting technology of titanium and its alloys was improved substantially by substituting a vacuum for the inert gas and using consumable electrodes made from the charge to be smelted and electromagnetic

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solenoid coils for stabilization of the arc and agitation of the molten metal pool in the furnace. The outgassing of the metal that takes place during vacuum smelting helped improve the mechanical properties of the ingots and the quality of their surfaces and improved their chemical homogeneity; contamination of the ingots by nonconsumable-electrode inclusions was eliminated, the melting rate rose considerably, and operating safety was improved.

A disadvantage of consumable-electrode work is the need to use expensive equipment to make these electrodes. A diagram of a vacuum-arc furnace with consumable electrode appears in Fig. 105.

#### The Electric Arc Burning in a Vacuum

It has been established by study of the conditions under which an electric arc burns in a vacuum that it burns with even greater stability at a residual pressure of  $1 \cdot 10^{-2}$  -  $1 \cdot 10^{-1}$  mm Hg than in air or a neutral-gas atmosphere, since the vacuum promotes formation of metal vapors and evolution of gases from the molten bath, thus making the atmosphere electrically conductive and supporting burning of the arc. It was possible to strike an arc without difficulty at a residual pressure of about  $5 \cdot 10^{-4}$  mm Hg.

The principal component responsible for the highest vapor concentration in smelting of titanium sponge appears to be the metallic reducing agent, usually magnesium. The ionization potential of titanium itself is considerably lower than those of other metals and the gases present as impurities in the titanium,

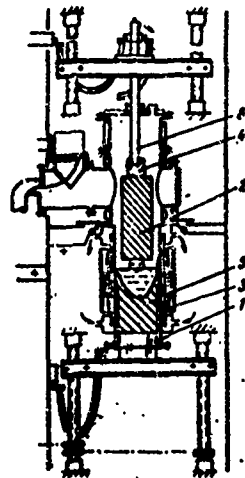


Figure 105. Diagram showing construction of vacuum-arc furnace with consumable electrode. 1) Water-cooled copper bottom; 2) consumable electrode; 3) water-cooled crystallizer; 4) electrode butt to which consumable electrode is welded; 5) titanium ingot; 6) electrode holder.

such as Mg, Mn, Fe, Si, C, H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>. The ionization potential of Ar, and especially than of He, are several times that of Ti. As a result, the electric arc burns less stably in He and Ar than in a vacuum. In an atmosphere of these gases, the maximum arc length obtainable with a tungsten electrode, a voltage of 50-60 V, and a current of 2000 A is 30-40 mm; in a vacuum under the same electrical conditions, arc length may reach 150-300 mm [4]. The possibility of arcing in a vacuum in the presence of titanium vapor alone has been demonstrated experimentally by repeated remelting of the same ingot [6].

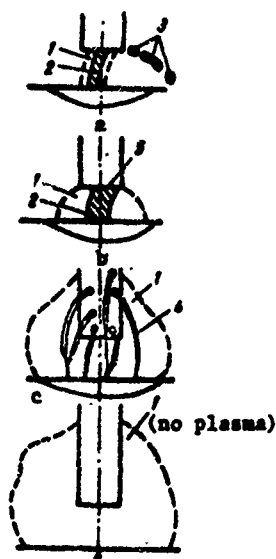


Figure 106. Shape of arc at various argon pressures. a) Noisy arc; argon pressure 340 mm Hg; b) quiet arc, argon pressure 110 mm Hg; c) wandering cathodic spot, argon pressure 30 mm Hg; d) argon pressure 4 mm Hg; 1) corona; 2) plasma; 3) droplets; 4) fine plasma; 5) broad cathodic spot.

Figure 106 [7] shows the changes in the outlines of an arc between a thoroughly outgassed titanium consumable electrode and a pool of molten titanium as the argon pressure is lowered. The instability of the arc in the 0.5-30 mm Hg pressure range is often regarded as a transition of the gas discharge into another physical form — the volume (glow) discharge. In volume discharge, the cathode is not softened, and the crucible walls are heated rather severely and may burn through. Simultaneously, the liquid-metal pool receives less and less heat and solidifies. The intensity of a volume discharge depends on a number of factors, most important among which are the pressure and composition of the gaseous phase. For argon, the lowest voltage at which a volume discharge arises is 25 V at residual pressures in the range from 0.25 to 5 mm Hg. For hydrogen, which ionizes under a higher voltage, the relationship is different: the 70-V voltage minimum at which a volume discharge appears corresponds to a pressure of

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about 0.6 mm Hg. On deviations from this value in either direction, the voltage at which the volume discharge arises increases sharply [7]. Because the principal component of the gaseous phase during smelting of titanium is hydrogen, the danger of glow discharge is reduced.

Figure 107 shows a diagram of the voltage drop in various zones of a vacuum arc discharge [8].

In an arc discharge, thermionic emission occurs on a small area known as the cathodic spot. The temperature on this zone for an arc burning in air varies over a broad range (from 2500 to 3000°C) and depends on a number of factors. The cathodic-spot temperature of an arc burning in a vacuum is lower than for an inert atmosphere, since the spot itself broadens as the pressure is lowered and the current density through it decreases.

The extent of the cathodic region of the arc discharge is very small and corresponds approximately to the electron free path, i.e., about  $10^{-4}$  cm at 1 atm. However, the voltage drop over this distance is 15-20 V.

The positive trunk of the arc is an electron-ion plasma at whose center the temperature reaches 5000°C or higher. The current in the trunk is carried for the most part by electrons, owing to their higher mobility as compared with ions. The voltage drop in the trunk under vacuum conditions is no more than a few volts. The positive trunk of an arc discharge terminates in the anodic region, in which the voltage drop is even greater than that in the cathodic region. A spot also forms on the anode, and its temperature is higher than that of the cathodic spot, since electrons striking the surface of the spot yield not only their kinetic energy, but also an energy equal to the electron work function. Anodic-spot temperature decreases slightly with decreasing pressure: for an arc between graphite electrodes, from 4200°C

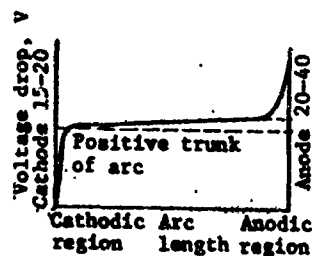


Figure 107. Diagram showing voltage drop in various zones of arc discharge in vacuum with graphite electrodes.

at 1 atmosphere to 3500°C at 0.1 atmosphere.

The anodic spot occupies a substantially larger area in a vacuum than in argon at a pressure of 1 atm. This promotes more uniform heating of the liquid metal pool surface and makes the pool deeper.

The residual pressure in the arc furnace also influences melting rate. The increase in melting rate during vacuum smelting is explained by the fact that the gases released from the electrode break up the surface film of molten metal on it and help eject the resulting fine droplets into the pool. The following theoretical smelting efficiencies — ratios of the actual electrode smelting rate to theoretical — have been found for titanium: 25% at an argon pressure of 1 atmosphere and 42% in a vacuum. The thermal efficiency of the arc furnace is also improved in vacuum operation by the smaller heat losses from the furnace working space.

Application of a longitudinal magnetic field across an electric furnace compresses the trunk of the arc and causes it to rotate, owing to the interaction of the solenoid electromagnetic field with the longitudinal field of the arc. The pool of molten metal also begins to rotate simultaneously.

The longitudinal magnetic field is set up by winding a solenoid on the crystallizer. The solenoid is supplied with direct current, e.g., from the current source that supplies the arc. Comparatively little power is used to supply the solenoid.

The arc should burn inside the solenoid or slightly below it. Use of a solenoid greatly reduces the danger of lateral parasitic arcing between the electrode and the crystallizer wall. Under the influence of the magnetic field, such arcs are also set in spiral rotation, which stretches them to the point at which they go out. Then the position of the anodic spot can be adjusted within certain limits by varying the angle of inclination of the solenoid axis to the crystallizer axis, without permitting the arc to transfer to the crystallizer wall. The compression of the main arc trunk by the solenoid magnetic field is also of

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assistance here. As the strength of the field rises, arc length can be increased without increasing the danger of lateral arcing.

The angular velocity of the molten pool is higher at its center than in its peripheral regions, and this helps mix the metal and distribute alloying additives more uniformly in the ingot.

Solenoid magnetic field strength has a strong influence on the depth of the molten metal pool. At first, pool depth rises with increasing number of ampere-turns, since the arc trunk and anodic spot become narrower in the magnetic field, heating is concentrated in the center of the pool, the fraction of heat going to the crystallizer walls is reduced, and mixing of the pool improves heat transfer between the upper and lower layers of the molten metal. As the magnetic field strength increases above a certain limit, whose value depends on crystallizer diameter, amperage, and other factors, the spinning of the molten metal pool becomes so rapid that heat transfer to the crystallizer walls increases markedly, pool temperature decreases, and the pool becomes shallower. Accordingly, the ingot surface also improves at first, but then becomes porous again [9].

Proper molten-pool agitation made it possible to pour a 75-kg T15A14V ingot in which the discrepancies between aluminum analyses made at 10 points spaced along the height of the ingot and in various horizontal cross sections amounted to 0.1%, i.e., were less than the limits of error of the analysis. The vanadium-content variations were even smaller [9].

Rotation of the molten-metal pool also improves ingot structure by preventing the formation of columnar crystals. It has been proposed that the direction of the current in the solenoid be varied to obtain stronger agitation of the molten pool. Recommendations as to the frequency of these reversals disagree. One source [10] indicates 2 seconds, while another<sup>(1)</sup> cites 3 minutes for an ingot 711 mm in diameter.

Apart from artificially superimposed magnetic fields, the electric arc is also strongly influenced by the intrinsic magnetic

Footnote (1) is on page 559.

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fields of the current cables, motors, transformers, etc. These fields, as well as heavy iron masses, act unilaterally on the arc, deflecting it from its normal position. It is therefore recommended that either a single tilting solenoid or two solenoids — a stationary unit wound on the crystallizer and a moving unit — be used to secure more precise regulation of the arc [8].

#### Electrical Conditions of Smelting

The manner in which the electrode is melted and depleted depends very strongly on the electrical conditions of smelting — voltage, current density, and arc length. Under normal conditions, the arc voltage is about 30 V, the current density at the electrode at least 10 A/cm<sup>2</sup> (at an ingot diameter of 300-400 mm), the arc is 20-25 mm long, and the bottom of the electrode is flat with slightly rounded edges. When the current density is inadequate, beads form at the edges of large-diameter electrodes as a result of rotation of the molten liquid layer on the electrode and freezing of the liquid metal at its outer margin. When the electrode's outer surface is strongly cooled, its low thermal conductivity makes the bottom of the electrode concave. With increasing voltage and arc length, the end of the electrode becomes more and more rounded and eventually spike-shaped.

The drops also form on the electrode and drop off in different ways depending on the electrical conditions of smelting. Given adequate current density and normal arc length, many fine droplets form on the end of the electrode and move across the end surface as they grow, thus averaging out the composition of the drop. At low current density, the droplets grow slowly but to large dimensions, closing the electric circuit themselves when the arc is short. The comparatively cold face of the electrode is then cooled even more strongly; the large cold drops of metal fall immediately to the floor of the pool and freeze quickly without having had time to mix with the molten metal. When smelted under such conditions, ingots containing high-melting alloying additives are extremely nonuniform in composition. Large cold drops of metal can also form at normal current density if the arc is too short or too long. The arc zone is cooled in the former case by

frequent short circuiting, and in the latter by formation of parasitic lateral arcs that heat the electrode above the melting zone. This lowers the power of the main arc, whose function is to provide the necessary heating of the metal drops.

The basic prerequisite for economical and stable furnace performance is maintenance of the shortest possible arc. However, its length is limited by the appearance of short circuits as the drops of liquid metal drain from the electrode onto the ingot.

Research results and practical data have shown that arc length should be held in the 30-40-mm range in a wide range of ingot diameters (50-600 mm), and should not in any event exceed the distance between the side of the electrode and the crystallizer wall.

The temperatures of the melting electrode face and the pool surface are independent of furnace power in the pressure range from 0.1-1000 mm Hg. A change in power is accompanied by a corresponding change in melting rate, which thus becomes a kind of built-in automatic controller of the furnace processes.

Measurements of electrode temperature in a titanium-smelting furnace yielded the following results: temperature of melting face of consumable electrode 1775°C, surface temperature of molten-metal pool 1850°C [11].

Electrode melting rate is directly proportional to current [9]. But, on the other hand, the melting rate may not be excessively high, since the bottom of the consumable electrode and the liquid pool must be outgassed simultaneously with melting. As for optimum current density, a number of circumstances must be considered in specifying it. From the standpoint of economy, it is desirable to have the highest possible current density and, consequently, furnace productivity. Moreover, the size of the molten-metal drops draining from the electrode increases with electrode current density, making it possible to work with a short arc without shorting across droplets. In turn, the shorter arc makes it possible to work at low residual pressures, which are desirable from the standpoint of improving ingot quality.

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Other conditions the same, a higher current density helps improve furnace productivity, increase pool volume, and improve ingot surface. However, as ingot diameter increases, conditions for withdrawal of heat from the crystallizer deteriorate, and for this reason the optimum current density, calculated for the crystallizer cross section or, which is the same thing, the ingot cross section, must decrease with increasing crystallizer diameter.

Below we list the recommended currents and current densities in arc furnaces for titanium smelting as functions of crystallizer diameter [12].

| Ingot diameter, mm | Current, A | Current density, A/cm <sup>2</sup> |
|--------------------|------------|------------------------------------|
| 100                | 2000       | 25.4                               |
| 200                | 4400       | 14.0                               |
| 300                | 6800       | 9.6                                |
| 400                | 9000       | 7.2                                |
| 470                | 12000      | 7.0                                |
| 620                | 20000      | 5.7                                |
| 850                | 24000      | 4.2                                |

These data are somewhat lower than those given in [1], which recommend current densities of at least 10 A/cm<sup>2</sup> for smelting out ingots 300-400 mm in diameter, i.e., currents of 7.0-12.5 kA, respectively. It is noted in [1] that the current densities presently in use still appear to be far from the optimum and, consequently, that there is much room for improvement of furnace productivity.

Toward the end of the melting process, conditions are adjusted to prevent the formation of "pipe" in the ingot and solidification of the metal in the form of coarse columnar crystals. To bring the pipe out to the top of the ingot, the wattage supply is gradually reduced and the number of ampere-turns on the solenoid is increased, or, in other words, agitation of the pool is stepped up to help it cool. Both procedures result in a shallower pool of molten metal. Toward the end of smelting, the pool may freeze completely [9]. The operation of extracting the pipe takes a rather long time, depending on ingot size; for example, 1.5 to 2 hours for an ingot 620 mm in diameter [13].

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To simplify pipe extraction, one of the patents<sup>(2)</sup> proposes that the top end of the consumable electrode be made (or welded up) with a diameter one-half to one-third that of the main body of the electrode and melted at a current representing about 15% of the nominal process current.

Figure 108 shows a typical heat-balance diagram for a vacuum arc furnace. It indicates that the efficiency of the arc furnace ranges from 30 to 50%, depending on its power, and may reach 65-70% in powerful furnaces [11].

The theoretical power consumption for smelting of titanium is 0.45 kW·h/kg, while the practical figure is about 1 kW·h/kg. Figuring on two remeltings and approximately the same consumption for auxiliary requirements, the total power consumption would come to 3-4 kW·h/kg [5, 6, 12].

#### Influence of Furnace Residual Pressure on Melting

According to practical data, titanium sponge contains an average of 0.3-1.0 liter of gases per kilogram. During melting, the furnace vacuum drops as a result of desorption of air and moisture from the consumable electrode and evolution of absorbed hydrogen and other gases. The release of adsorbed gases, moisture, and other volatile impurities begins when the vacuum is created in the furnace and continues until the temperature has reached about 400°C [14]. At 400-500°C, the titanium begins to chemisorb gases trapped in its pores, which undergo practically no desorption at the temperatures of the solid state. The evolution of water of crystallization from the magnesium chloride is complete at 500-590°C; some of it is removed by the pump, and the rest reacts with the titanium.

Footnote (2) is on page 559.

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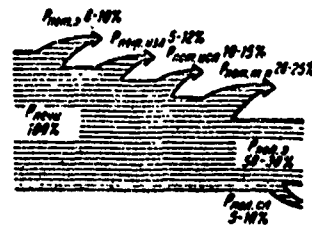


Figure 108. Typical heat-balance diagram for vacuum arc furnace.  $P_{\text{loss.e}}$ ) radiant electrode loss heat flux;  $P_{\text{loss.r}}$ ) ingot radiant heat flux;  $P_{\text{loss.e}}$ ) metal-evaporation losses;  $P_{\text{loss.h.c}}$ ) heat conduction losses in body of ingot;  $P_{\text{u.e}}$ ) useful power consumed in melting electrode;  $P_{\text{u.i}}$ ) useful power dissipated in ingot.

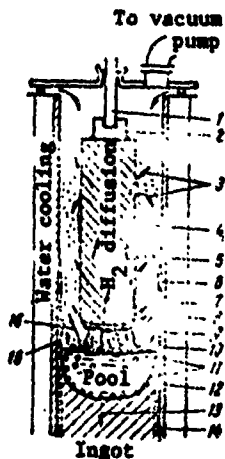


Figure 109. Diagram of process in which gases and vapors are evolved during melting of consumable electrode. 1) Electrode holder; 2) mount; 3) evolution of  $H_2O$ ,  $O_2$ ,  $N_2$ ; 4) condensate of Mg and  $MgCl_2$ ; 5) Mg, Mn, Cr,  $MgCl_2$  and other vapors; 6) condensate of Mg and  $MgCl_2$ ; 7) condensate of Mn and Cr; 8) evolution of Mg,  $MgCl_2$ , and  $H_2$ ; 9)  $MgO$  and  $Mg_3N_2$  fall back into pool; 10) crown; 11) Mg and  $H_2$  bubbles; 12) pores filled with  $MgCl_2$ ,  $MgO$ ,  $Mg_3N_2$ , Mg, Mn, Cr, etc.; 13)  $H_2$  diffusion; 14) clearance between ingot and crystallizer; 15) secondary vaporization of Mg,  $MgCl_2$ , Mn, Cr, etc.; 16) removal of Mg,  $MgCl_2$ ,  $H_2$ ,  $MgO$ ,  $Mg_3N_2$ .

electrode always releases larger quantities of gas as it melts. The unequal gas contents in different zones of the ingot give

Vigorous evolution of gases from the molten metal is observed during melting in practice. Hydrogen bubbles also form in addition to the bubbles of magnesium vapor, since the solubility of hydrogen in titanium decreases with rising temperature. Gases and impurities of other metals dissolved in the molten titanium may diffuse into the magnesium-vapor bubbles that are generated. The vapors of magnesium and other impurities with high vapor pressures create a protective atmosphere over the molten pool and the melting part of the consumable electrode. They react with air, some amount of which invariably gets into the furnace. To some extent, the oxides and nitrides formed in this process condense in the cold zones of the furnace, and some of them enter the molten metal pool.

Hydrogen comprises about 96% of the total amount of gases liberated during melting [8, page 236]. As the consumable electrode melts, some of the hydrogen diffuses into the dense, cooler part of the ingot and into the upper zones of the consumable electrode. As a result, the top end of the

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rise to differences in the mechanical properties of the metal — primarily its impact strength — in these zones. Vacuum annealing of the ingot improves its impact strength.

Figure 109 presents a diagram of the processes in which gases and vapors are released during melting of a consumable electrode.

Usually, the residual pressure in the furnace is measured at the rim of the crystallizer. It has been established experimentally [15] that the pressure in the arc zone may be many times that at the crystallizer rim.

The pressure gradient in the crystallizer depends basically on the following factors: the quantity of gases released in the arc zone, the relationship between the cross sections of the crystallizer and the electrode, the distance from the pool surface to the crystallizer rim, and pressure fluctuations in the space above the crystallizer. Since these conditions are different in each operating furnace, it is quite natural for the pressure gradient in the crystallizer to show appreciable variations.

According to the calculated data given in [11], the pressure in the melting zone at a furnace working chamber pressure of 10  $\mu\text{m Hg}$  and a melting rate of 15 kg/min is 40-70  $\mu\text{m Hg}$ , without consideration of leakage into the furnace.

Ye.I. Morozov and I.A. Prostov [2] studied the influence of residual pressure on the quality of titanium and titanium-alloy ingots. In the case of low-vacuum melting, the hydrogen content in the technical titanium dropped to 0.0053% as against the 0.0078% for melting in helium at 160 mm Hg, and the impact strength of the metal rose from 2 to 5  $\text{kgf}\cdot\text{m}/\text{cm}^2$ . The impact strength of the metal rises steadily as the vacuum is hardened further; terminal elongation and necking ratio also increase, while strength decreases slightly.

Hardening the vacuum during melting of VT3, VT3-1, and VT4 alloys does not increase impact strength. Mechanical characteristics improve substantially only on the transition from helium to vacuum. It appears that the alloying metals in these alloys influence their mechanical properties to a greater degree than does

hydrogen.

According to [16], the mechanical properties of forgings made from titanium ingots melted out in a high vacuum were superior: hardness dropped by 9%, ultimate strength was down 3.5%, and the necking ratio increased by 4.5%.

Experiments conducted by the U.S. Bureau of Mines indicated that a residual pressure of the order of  $10^{-4}$  mm Hg caused no appreciable increase in the vaporization of titanium during melting, since the vapor pressure in the zone of the anodic spot and the molten pool is substantially higher than that in the interior of the furnace.

Specific power consumption was 0.86 kW-h/kg for melting under a pressure of 50-100  $\mu$ m Hg, and 0.74-0.78 kW-h/kg at a pressure of 0.5  $\mu$ m Hg. Thus, despite the 100-200-fold pressure decrease, power consumption was lowered by only 13% [17].

When alloys containing components with comparatively high vapor pressures, such as manganese, chromium, etc., are smelted out in a hard vacuum, they undergo partial vaporization, which causes departures from the desired alloy composition.

High-vacuum smelting requires the use of powerful vacuum pumps, and this increases the cost of the vacuum unit. The low furnace residual pressure may cause more air to leak into the furnace. On the other hand, operation of the furnaces at a pressure of 0.1-1 mm may produce a glow discharge that throws the arc onto the crystallizer and burns it through. For these reasons, the optimum furnace pressure during smelting is put at  $10^{-2}$ - $10^{-3}$  mm Hg [2].

One of the conditions that helps create a good vacuum in the furnace is thorough cleaning of its internal surfaces and degasification of the furnace before smelting. It is recommended that degasification be carried out in a vacuum while hot water is being run through the furnace water-cooling system; it can be accelerated by setting up a brief glow discharge in the furnace [18]. Since titanium sponge is hygroscopic to a certain extent, pressed consumable electrodes should be dried thoroughly at about 150°C

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#### Smelting of Titanium Alloys and Sodiothermic Titanium

The process of melting a consumable electrode in a water-cooled copper crystallizer is characterized by comparatively small dimensions of the molten-metal pool and the difficulty of overheating the pool to any substantial degree. The pool could be overheated by reducing the heat losses or increasing the power of the electric arc, but at the current densities normally used, an increase in arc power results for the most part in an increased melting rate of the consumable electrode, with an insignificant increase in the overheat. These two circumstances complicate the smelting of titanium-alloy ingots with uniform chemical composition.

Titanium is alloyed with elements that differ from it substantially in both directions as regards melting point and density. For example, molybdenum has a melting point of 2620°C and a density of 10.23 g/cm<sup>3</sup>, aluminum 660°C and 2.7 g/cm<sup>3</sup>, respectively, and tin 232°C and 7.3 g/cm<sup>3</sup>.

Elements with properties similar to those of molybdenum do not have time to dissolve in the molten titanium pool before it begins to crystallize; tin cannot be smelted out of the consumable electrode before the base metal melts. In either case, the ingot will have nonuniform chemical composition. In smelting titanium alloys, therefore, it is advisable to alloy the titanium not with individual elements but with master alloys. It is expedient to melt high-melting alloying elements together with the aluminum used in most titanium alloys, since this will help lower the melting point of the master alloy and its density, while low-melting alloying elements — aluminum and tin — may be fused with high-melting elements, with titanium as the prime example. Various methods may be used to prepare the master alloys: vacuum induction furnace melting, melting in the vacuum arc furnace with nonconsumable and consumable electrodes, and aluminothermics.

Along with the use of master alloys to smelt ingots containing high-melting additives, it is recommended that the cathodic

spot be strongly focused to obtain local overheating of the liquid drops forming on the face of the electrode and to produce the deepest possible liquid metal pool. To do this, it is necessary to melt in a short arc of increased power. This shortens the melting time, and the specific power consumption remains about the same as in smelting under ordinary conditions [8, page 236].

As a rule, current is set proportional to ingot diameter in smelting titanium alloys. This follows from the conditions for maintaining a constant ratio of pool depth to ingot diameter. For most alloys,  $I = KD$ , where  $K = 300$  A/cm, which results in approximate equality of the ingot diameter to the depth of the molten metal pool [19].

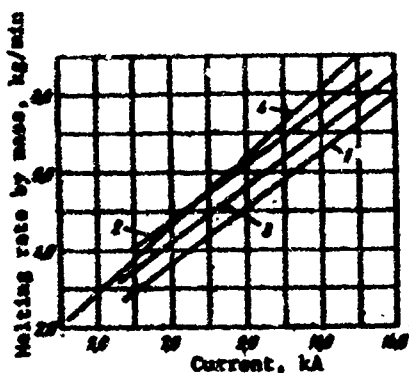


Figure 110. Average mass melting rate of titanium-alloy ingots of various sizes as a function of current. 1) Electrode diameter 460 mm, ingot diameter 630 mm; 2) electrode diameter 280 mm, ingot diameter 456 mm; 3) electrode diameter 280 mm, ingot diameter 380 mm; 4) electrode diameter 200 mm, ingot diameter 380 mm.

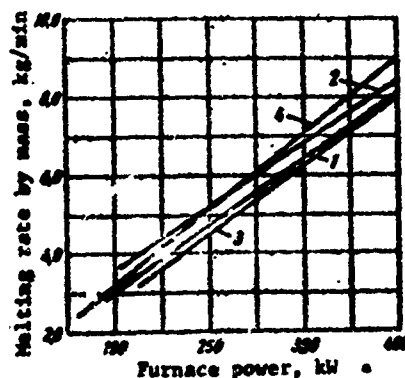


Figure 111. Average mass melting rate of titanium-alloy ingots of various sizes as a function of arc-furnace power. 1) Electrode diameter 456 mm; ingot diameter 630 mm; 2) electrode diameter 280 mm, ingot diameter 456 mm; 3) electrode diameter 280 mm, ingot diameter 380 mm; 4) electrode diameter 200 mm; ingot diameter 380 mm.

Figure 110 shows the melting rates of alloy ingots up to 620 mm in diameter as they depend on current, while Fig. 111 shows the dependence on furnace power

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[13, page 266]. The alloy melting rates given in Fig. 110 are approximately half those given in [1] for the melting rates of technical titanium.

Smelting of manganese-containing ingots presents certain difficulties, since manganese is vaporized as the consumable electrode melts, condensing on the crystallizer walls and concentrating in the outer layers of the ingot. Manganese vapor promotes the development of glow discharges. In view of this fact, the first remelting of alloys containing manganese is usually carried out in a vacuum, and the second under an argon or argon-helium pressure of 40-200 mm Hg [19].

Large-diameter ingots can be melted at comparatively low voltages without detriment to arc stability. This is because of the smaller voltage drop in the consumable electrode and the smaller linear electrode melting rate for larger diameters. The melting process is quieter, and it becomes possible to shorten the arc gap and prevent local short circuits that result from spattering. The yield of acceptable 620-mm-diameter ingots was about 90%, or 5% higher than for 380-mm ingots [13, page 266].

The influence of chlorine present in titanium sponge on the course of the melting process was studied in [20]. It was found on smelting OT4 and VT1-2 alloy ingots containing 0.06-0.12% Cl that a sponge content of up to 0.1-0.12% Cl has no effect on melting (spattering, outgassing, ionization, etc.), crystallizer cleanliness, or melting-cycle time.

Chlorine contents ranging from 0.06-0.08% in type TGO sponge and from 0.08-0.12% in type TG1 sponge had no influence on the mechanical properties of the ingot or sheet produced from it.

Certain distinctive effects are observed when sodiothermic titanium powder is melted. The sodiothermic titanium used for the test melts contained 30-40% of fractions smaller than 1.25 mm. When this metal was melted, the higher contents of sodium chloride, hydrogen, and absorbed gases as compared with magnesiothermic sponge caused considerable spattering of the metal as a result of vigorous evolution of gases. A result was lower arc stability

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and the frequent appearance of glow discharges. The strong tumbling and spattering of the liquid metal pool and dissociation of the sodium chloride coated the surfaces of the crystallizer, vacuum chamber, and vacuum system with splatterings of titanium and deposits consisting of sodium chloride, titanium dust, and metallic sodium. The last two components are explosively inflammable when the furnace is opened to permit contact with atmospheric moisture.

Preliminary degasification of briquettes made from sodiothermic powder was detrimental to the mechanical properties of the final ingots. It was found more advantageous to prepare the consumable electrodes by surface-melting the briquettes, without degassing, in an arc furnace operating at reduced power with a nonconsumable electrode. Remelting of the resulting ingots produced metal whose mechanical properties satisfied the technical specifications for magnesiothermic titanium ingots [21]. Ethyl alcohol was introduced into the cooled furnace after melting to bind the metallic sodium that had condensed inside the furnace into sodium alcoholate, which does not react with atmospheric moisture when the furnace is opened.

Titanium-alloy ingots are usually remelted to ensure constancy of chemical composition and mechanical properties. Furnaces designed to accommodate both meltings can be used for this purpose. The object of the first of the two meltings is to remove the metallic reducing agent, its chloride, and hydrogen, and to establish a more or less uniform distribution of the alloying additives. The surface quality of the first ingot is of no particular importance. The purpose of the second remelting is to improve the uniformity of alloying-additive distribution and produce a surface with no pores or blisters in order to minimize weight losses when the ingot is dressed; it sometimes makes it possible to dispense with dressing altogether. In the second remelting, casting defects usually form at the bottom of the ingot, since the molten metal drains onto the cold floor at the beginning of melting. To eliminate this shortcoming and protect the floor from burning through, a primer (template) of metal of

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the same composition as the ingot being smelted is usually placed on the floor.

It is most important to determine the influence of remelting on the mechanical properties of titanium. It has been established by a laboratory of the US Bureau of Mines that remelting of titanium is not, per se, detrimental to the quality of the metal. The same ingot was remelted thirty times using the ingot obtained in the previous melting as a consumable electrode for the subsequent melting. The hardness of the last ingot was 30 Brinell units higher than that of the first; this corresponds to an increase in ultimate strength of about  $0.3 \text{ kgf/mm}^2$  per remelting [22]. This problem was studied in greater detail in [8, page 236]. Technical titanium was melted at a residual pressure of  $1 \cdot 10^{-2}$ - $5 \cdot 10^{-3}$  mm Hg. First, two ingots 100 mm in diameter and weighing 5 kg each were smelted from briquettes 70 mm in diameter in a laboratory furnace; these ingots were then remelted into ingots 130 mm in diameter. A single ingot 150 mm in diameter was produced from two of these ingots in a semiindustrial furnace and used in the fourth step to smelt out an ingot 176 mm in diameter. Between remeltings, the ingot surfaces were cleaned with a wire brush to remove sublimates. In addition, one ingot was roughed off to a depth of 3 mm after each remelting to eliminate the influence of gases and moisture on its properties. Another ingot was smelted out with three intermediate forgings between remeltings. It was found that the second and last remeltings were quite detrimental to the ingot's properties. At the same time, the ingot that had been smelted with four remeltings and intermediate roughing off of the surface after each remelting had practically the same properties as the ingot obtained after one remelting. The greatest losses of ductility and toughness were reported for the ingot made with four remeltings and intermediate forging and roughing. In this case, hydrogen content also increased.

These results imply that when air leakage is controlled, the furnace is thoroughly cleaned before melting, and the ingot surface is roughed, the metal is subject to practically no contamination during remelting. If the ingot is not dressed before

remelting, the moisture introduced by hygroscopic sublimate residues on the surface of the ingot will contaminate it with oxygen. If the ingot is forged between remeltings, the gases absorbed from the atmosphere have time to penetrate so deep into the ingot that subsequent dressing does not ensure complete removal of the gas-enriched layer.

The results cited above agree with practical data to the effect that repeated remelting of a titanium ingot without the measures enumerated above increases oxygen content by approximately 0.04%; this corresponds to an ultimate-strength increase of 3-5 kgf/mm<sup>2</sup> [13, page 282].

However, double remelting of the ingot in the same furnace without lifting the vacuum has practically no effect on its mechanical properties.

The smelted ingots are machined: the end surfaces are trimmed off and the sides are roughed. As a result, the useful yield usually comes to 85-90%, reaching 95% for large ingots [13, page 266]. To eliminate the need for roughing of the ingots, it has been proposed that they be surface-melted, e.g., with a nonconsumable electrode.

The finished ingots must be quality-controlled ultrasonically or by some other method to detect structural defects.

#### Preparation of Consumable Electrodes

The following basic requirements are made of consumable electrodes for smelting of titanium and titanium-based alloys [8, page 221]:

- a) adequate mechanical strength, which eliminates the possibility of electrode breakage during shipping or melting;
- b) limited warping, so that the clearance between the side of the electrode and the crystallizer walls will be uniform;
- c) absence of low-melting or readily vaporized additives on the outer surface of the electrode, since otherwise these additives might melt out of the electrode or vaporize with formation of stray arcs between the electrode and the crystallizer wall;

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d) the lowest possible electrical resistance, to reduce the influence of electrode length on furnace electrical parameters;

e) the highest possible electrode density, to reduce electrode length and, accordingly, furnace height.

There are several ways to prepare consumable electrodes: a) sintering in a furnace with a nonconsumable electrode; b) sintering in containers; c) block pressing in a vertical or horizontal pressform, with subsequent joining of the blocks into a consumable electrode by welding; d) hydrostatic pressing of blocks, with subsequent welding of their components; e) pressing the electrode through an extrusion die.

Arc-furnace sintering with a nonconsumable electrode, usually of graphite, is used to make consumable electrodes when the appropriate presses are not available. The charge is fed mechanically from a hopper to the graphite electrode. The sponge is fed in rapidly for sintering so that there will be time only for sintering or slight surface melting. Since the time of contact between the material to be sintered and the graphite is short, there is practically no carburization of the material [2]. Melting takes place at a voltage of 45-50 V and an arc length of 200-300 mm; the melting rate is 150-230 kg/h; specific power consumption is 1.1-1.6 kW·h/kg [21].

This method is obviously unsuitable for preparation of electrodes for ingot smelting.

Container sintering of consumable electrodes eliminates the need to use presses; one method is of a certain interest in that it makes it possible to introduce up to 90% of lump scrap into the electrode. This method will be examined in Chapter 21.

Rectangular or cylindrical blocks are produced by pressing into cavity dies and then welded together to form an electrode of the desired length. Reverse-tapered cavity molds are used to make the blocks, since they give almost uniform specific pressures over the entire cross section of the block and make it easier to extract. The lower end of the ram usually has a conical projection, so that a corresponding depression is formed in the top of the

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block to receive alloying additives. This eliminates the possibility of the additives melting out when the electrode is heated in the furnace. A single pressing portion of sponge may weigh about 3 kg and the total weight of the block may range up to 35 kg; the blocks range to 650 mm in height, and their densities vary from 3.4 to 3.5 g/cm<sup>3</sup>. The specific pressure must be about 3.5 tons/cm<sup>2</sup> [8, page 221]. The blocks or sectors are welded together with titanium wire in an argon atmosphere in a rather time-consuming operation.

Figure 112 [23] shows a 950-kg consumable electrode welded up from individual blocks.

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Figure 112. Consumable electrode welded up from individual blocks.

high electrical resistance at the points of contact between blocks has been tested. When current flows, these points heat up rapidly to 800-900°C, which is enough to sinter the blocks together securely. An advantage of this method is the fact that the blocks are heated gradually, with elimination of gases and water vapor at 300-400°C. However, the same gases are absorbed in substantial amounts by the molten titanium pool when the electrode is

As a technique for welding the blocks together to form a consumable electrode, it has been suggested that they be placed in steel rings, which would then be inserted into a horizontal sealed argon-filled pipe. The rings would then be rotated and traversed for positioning under a consumable or nonconsumable welding electrode. The maximum dimensions of the electrodes produced by welding the blocks in the tube: length up to 3 m, diameter up to 250 mm, or diagonal up to 280 mm.

A method of contact block sintering based on the rather

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degasified in the furnace. The current needed to sinter an electrode from blocks 80-100 mm in diameter must be about 3000 A, and at least 6000 A for a 150-mm diameter [8, page 221].

In the industry, blocks are pressed hydrostatically. After preparation for pressing, the charge is poured into a waterproof elastic bag, which is placed in the press container; the container is fitted with a quick-seal cover and filled with water or some other liquid to develop the required pressure. The advantages of hydrostatic over ordinary pressing are less stringent requirements as to the shape of the pieces of material pressed by this method and the possibility of obtaining stronger and denser compacts in rather large sizes. For example, compacts up to 330 mm in diameter and 1000 mm high are made by this method [23].

The most productive method of preparing consumable electrodes is that of extrusion through a tapered pressform (Fig. 113) [12; 8, page 221]. Before pressing is started, the tapered die is fitted with a bottom plate. When the initial briquette has been formed, the plate is removed from the die. Subsequent compacting takes place as a result of the electrode's resistance to upsetting as it is extruded down through the die. A disadvantage of this pressing method consists in the fact that specific pressure at the walls of the pressform is several times that at the center of the electrode. As a result, the sponge in the central core of the electrode moves ahead of the sponge in the outer layers, so that the outer layers come under tensile stresses and tend to crack; the strength of the electrode is lowered, and this may cause it to break in the furnace. To eliminate this effect, the electrodes are strength-tested before insertion in the

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Figure 113. Diagram showing principle of tapered pressform for extrusion of consumable electrodes. 1) Tapered die; 2) bearing ring; 3) ram; 4) press crossbar.

furnace. If necessary, the specific extrusion pressure is raised. It is usually about 3-4 tons/cm<sup>2</sup>, and the final electrode has a density of about 7.5 g/cm<sup>3</sup> and a tensile strength of 12-15 kgf/cm<sup>2</sup>. Specific extrusion pressure is lowered as the diameter of the consumable electrode increases. For example, electrodes 450 mm in diameter can be extruded under a specific pressure of about 2 tons/cm<sup>2</sup>. The possibility of lowering the specific pressure results from the smaller circumference-to-area ratio of the electrode and, consequently, the lower friction of the electrode against the wall of the pressform as it is extruded. This extrusion method has certain disadvantages. Horizontal presses are normally used for it, and this makes it difficult to introduce alloying additives into the core of the electrode. Long (3-5-meter) electrodes are noticeably warped. Since much of the extrusion effort is expended in overcoming friction, high-power presses are required.

However, these disadvantages of tapered-form extrusion are offset by a substantial advantage: direct formation of final consumable electrodes of the desired length; this factor is responsible for the extensive industrial use of this method.

To permit use of presses with smaller capacities for preparation of consumable electrodes, it has been proposed that the material be pressed through a tapered die with subsequent sintering. In this method, the electrodes are pressed at specific pressures of 0.7-1.4 tons/cm<sup>2</sup>, after which they are sintered in a vacuum for 12 hours at 950°C. The hydrogen content in the electrode is reduced simultaneously, e.g., from 0.020 to 0.006%.<sup>(3)</sup>

Magnesiothermic titanium sponge consists of comparatively large pieces; for this reason, certain difficulties are encountered in obtaining uniform distribution of the alloying additives in the consumable electrodes. These difficulties are further aggravated by the comparatively small size of the molten metal pool in the water-cooled crystallizer of the arc furnace. It has been established that even low-melting alloying additives (such as aluminum) do not have time to coalesce with the titanium during heating of the consumable electrode above the melting zone.

Footnote (3) is on page 559.

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Obviously, the uniformity of alloying-additive distribution in the consumable electrode and, consequently, in the final ingot as well, must stand in a certain relationship with the volume of the molten pool in the arc furnace. The volume variation of the titanium pool during the course of melting was determined in the following way: holes were drilled at various heights on the consumable electrode and pieces of a foreign metal were inserted into them; these pieces did not have time to melt, and sank to the floor of the pool. Then a macrotemplate was cut out of the ingot and not only the depth of the pool, but also its shape were determined from the positions of the foreign-metal fragments in it. Manganese was used as the control metal in one of the studies [24], and tungsten in another [8, page 221]. Figure 114 [8, page 221] shows the mass change of the molten-metal pool as an ingot formed in a crystallizer 250 mm in diameter. At the beginning of melting, owing to the strong cooling of the floor plate, the bath was shallow and flat. As the ingot grew, the bath became deeper and its vertical section came to resemble a parabola.

The corresponding calculations, which were confirmed in practice, led to the conclusion that it is unnecessary to mix the alloying additives intimately with the portion of sponge placed in the container to press a consumable electrode, provided that the sponge loaded in a single dose stands in a certain ratio with the mass of the molten pool in the furnace. It was assumed at first that the portion of charge might range up to 0.5-0.8 of the molten-pool weight. Mathematical elaboration and an experimental test showed that satisfactory ingot homogeneity is obtained after the second remelting when the molten-pool volume is three or more times the volume of the portion of charge being pressed at one

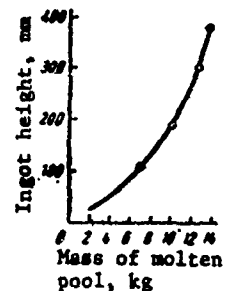


Figure 114. Variation of mass of molten-metal pool with ingot height during melting in a crystallizer 250 mm in diameter at an arc voltage of 29 V and a current of 3100 A.

time [8, page 221]. To eliminate composition nonuniformity at the bottom of the first-remelting ingot, it is recommended that it be turned over before the second remelting. Since this is impossible in present-day furnaces designed for double remelting without opening, the portion of charge should amount to about 0.2-0.4 of the molten-pool mass.

#### Design of the Vacuum Arc Furnace

The basic elements of the arc furnace (see Fig. 107) are the shell, the crystallizer that lines it, the electrode-transport mechanism, the vacuum system, and the electric power source. The type of furnace is usually indicated by the type of electrode used — consumable or nonconsumable — and by the type of crystallizer: with elevator or fixed bottom. When an elevator-bottom crystallizer is used, the ingot is lowered with the floor of the crystallizer as it builds up, with the molten-pool level in the crystallizer remaining constant. Constant level offers a certain convenience — the condensate, which consists basically of magnesium and magnesium chloride, settles above the level of the molten pool and thus does not interact with the molten metal. However, the crown of the ingot is often extracted together with the ingot. If, on the other hand, the crown is broken off, the resulting space fills with molten metal and a floathead forms.

During melting in a fixed-floor crystallizer, the pool level rises steadily, reaching the layer of condensate, some of which evaporates and is redeposited at a higher level, while some of it is cast into the molten metal, spoiling the surface of the ingot. Condensate usually forms in appreciable quantities during the primary melting; in the second remelting, therefore, it does not affect the ingot surface.

Thus, the advantage of crystallizer smelting with extraction is a minor one. At the same time, this melting technique complicates arc-furnace design and makes it difficult to control smelting. Quite frequently, the ingot jams in the crystallizer, making it necessary to shut down the furnace.

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As we noted above, titanium-alloy ingots are usually melted twice. To reduce furnace height, the first-remelting ingots are made with one-half or one-third the weight of the final ingot, and then these intermediate ingots are welded under argon outside the furnace or in the furnace itself into a single consumable electrode, which is remelted. Usually the stand with the crystallizer is placed on a trolley, which is rolled out from under the furnace when the first remelting has been completed and the ingot has chilled; the second-remelt crystallizer is then placed on the trolley, the first-remelt ingot is inserted into it, the trolley is rolled into position under the furnace, the crystallizer is installed, the furnace sealed, the first-remelt ingot welded to the electrode holder, and the second remelting begun. The second-remelt crystallizer is usually somewhat larger in diameter than the first-remelt ingot (the clearance between the electrode and the crystallizer wall should be about 50 mm on a side).<sup>(4)</sup>

In the furnaces that were used until quite recently to smelt titanium and titanium alloys, no more than 40% of the operating time was actually spent in the melting phase. The rest of the time was taken up by loading and unloading the furnace, pumping it out, cooling the ingot, and other auxiliary operations. Recent furnace-design improvements have substantially increased the utilization factor. This has been done by combining the two remeltings in a single furnace without breaking vacuum. The two remeltings take place successively with only a short pause between them. The ingot smelted out in the first remelting is not removed from the furnace. The electrode butt left after melting is dropped into the molten pool and the first-remelt ingot is welded to it. Then the ingot is raised into the furnace chamber, the chamber is separated from the crystallizer by a vacuum slide, the larger-diameter crystallizer is brought into position and evacuated, and then the vacuum lock is opened for the second remelting. The second-remelt crystallizers are also fitted with vacuum slides that make it possible to disconnect the crystallizer from the furnace with the hot ingot inside it and resume melting without waiting for the ingot to cool. A diagram showing the construction and Footnote (4) is on page 559.

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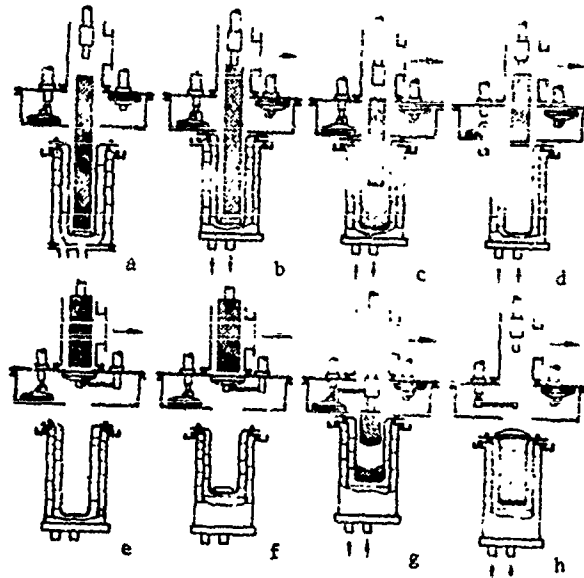


Figure 115. Diagram illustrating construction and operation of double-remelting furnace. a) Consumable electrode installed in first-remelting crystallizer; b) consumable electrode welded to holder; c) first-remelt ingot smelted out; d) first-remelt ingot welded to holder and elevated into furnace; e) furnace closed at bottom with vacuum slide; f) second-remelt crystallizer installed; g) second-remelt ingot smelted out; h) second-remelt crystallizer with ingot in it sealed with vacuum slide and disconnected from furnace to make room for installation of first-remelt crystallizer for next melt.

operation of such a furnace appears in Fig. 115. In this case, about 80% of furnace time is utilized.

The two remeltings may also be carried out without changing the crystallizer. In this case, the crystallizers are arranged one above the other. The first remelting takes place in the upper crystallizer, which has an elevator bottom. After the resulting ingot has been welded to the electrode holder, the bottom is lowered to the bottom of the lower crystallizer, in which the second-remelt ingot is smelted [26-28]. The more complicated furnace design required to accommodate two crystallizers has apparently been the reason why these furnaces have not come into extensive use [11].

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In large furnaces, the crystallizer diameters range up to 600-970 mm, and the ingots produced weigh as much as 10 tons. Such furnaces operate at currents up to 36 thousand amperes [144]. There is a trend toward even larger ingot masses. For example, it has been reported that technical data are available for the design of furnaces capable of making titanium ingots up to 1270 mm in diameter and weighing up to 18 tons [140].

As the ingots become larger, certain difficulties arise in clamping them before rolling. It would therefore be expedient to produce large ingots of rectangular or even oval cross section. It would be practically impossible to form rectangular ingots in arc furnaces; oval ingots could be smelted out after difficulties associated with properties of the melt and making the required crystallizers have been overcome. Rectangular titanium and titanium-alloy ingots could be smelted out in the electric slag furnaces that will be described below.

The furnace crystallizer is usually made of copper because of its high thermal and electrical conductivities. Recommendations as to the wall-thickness ratio of the crystallizer vary: 5-7 mm [5], 8-18 mm [29], and, recently, 40-50 mm [50].

Conflicting trends must be taken into account in determining the ratio between the cross sections of the consumable electrode and the crystallizer. To shorten the electrode and, consequently, reduce furnace height, and to lower thermal emission from the molten pool, the electrode cross section should be as close as possible to that of the crystallizer. On the other hand, in order to reduce the danger of parasitic lateral arcing, facilitate centering of the consumable electrode, and accelerate evacuation of gases from the crystallizer, this clearance should be as large as possible. It has been established in practice that the clearance between the electrode and the crystallizer should be no less than the length of the arc, i.e., 40-50 mm on a side for an arc 30-40 mm long.

The design of the crystallizer's water-cooling jacket must ensure the absence of vapor films at the interface between the water and the cooled surface, since the low thermal conductivity

of such films may cause the crystallizer walls to overheat and melt through. The flowrate of the water used to cool the crystallizer usually runs into the hundreds of liters per minute and is adjusted so that the exit water temperature is 10-20° higher than that at the entrance. The final temperature of the water should not exceed 40-45°C, since salts begin to deposit on the crystallizer walls at 45°C and sharply reduce their thermal conductivity. For the case of a closed system with softened water, the initial temperature is usually 15-20°C, but the final temperature may be raised to 50-60°C and higher.

A considerable amount of the power supplied to the furnace is expended in heating the furnace cooling water. The crystallizer — especially where its wall contacts the ingot — is the part of the furnace that is most heavily heat-stressed. Here the maximum heat flux (on the inner wall) may reach  $3 \cdot 10^6$  kcal/(m<sup>2</sup>·h), averaging  $(0.3-0.8) \cdot 10^6$  kcal/(m<sup>2</sup>·h); above the metal level, i.e., in the zone of the arc, the heat load is much smaller [ $(0.4+0.6) \times 10^6$  kcal/(m<sup>2</sup>·h)]. When the water moves at speeds greater than 1 m/s in the crystallizer, removal of heat from its walls can be provided for with an ordinary free-flow cooling system. At lower speeds, heat transfer will be effected by ebullition [30]. Heat representing approximately 80% of the furnace power may be taken off through the crystallizer. To increase the coefficient of heat transfer from the crystallizer walls to the water, the latter must flow through at several meters per second [2].

Use of a pressurized water jacket to cool the crystallizer presents a certain hazard, since a large amount of water might enter the furnace in the event of burning through of the crystallizer walls.

With the object of improving operating safety with water-cooled crystallizers, a published proposal has called for abandonment of the internal-water-jacket principle and use of an external water spray for evaporation cooling of the crystallizer.<sup>(5)</sup> For sprinkler cooling, the crystallizer is wrapped with a fine wire screen, which ensures uniform distribution of the water over

Footnote (5) is on page 559.  
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the crystallizer surface to be cooled. Experiments in which a crystallizer of this design was tested gave encouraging results [11]. When the crystallizer wall was intentionally burned through, with temperatures reaching 800-900°C at the point of the perforation, the water begins to flow around this point and only air, and no water, enters the crystallizer. The pressure rise in the furnace that results from this kills the arc and thus reduces the possibility of explosion.

An Na-K alloy that is liquid at room temperature was tested as a crystallizer coolant with a view to improving the explosion-proofness of the furnace.

The Na-K alloy is an extremely active substance, and, although the hazards associated with it may be eliminated, its use as a coolant complicates the equipment and makes it more expensive. However, practical use of this cooling system for titanium smelting has been reported [141].

Several hundred ingots ranging in diameter from 125 to 460 mm were smelted out in an arc furnace equipped with a cooling system of this type. The crystallizer burned through during one of the smeltings, but no explosion followed. The resulting ingot was checked for sodium and potassium contents in its surface layers. It was found that the color of the metal differed to a depth of 1.3 mm from that of the ingot's core, but sodium and potassium could not be detected in this surface layer. The ingot was spoiled -- not to mention damage to the furnace -- when a similar breakdown occurred in a water-cooled system [31].

The rod to which the consumable electrode is secured consists of two concentric pipes. Cooling water is supplied through the inner steel pipe, and electric current through the outer pipe which is made of copper for small furnaces or steel in large ones. The rod enters the furnace through a sliding vacuum seal. A consumable-electrode butt 200-300 mm long is screwed onto the lower end of the rod. The butt and the consumable electrode are welded together by striking an arc between them. The rod is raised and lowered with the aid of a screw or hydraulic drive.

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In the normal course of smelting, the rate of consumable-electrode feed is in the tens of millimeters per minute. To eliminate short-circuiting and quench lateral arcs, the electrode must be able to move two or three times as fast; in addition, the transport mechanism must have the shortest possible response lag and no backlash. These conditions are met by a two-speed reduction gear with electromagnetic clutches that has been developed in the USSR and by two-speed hydraulic or hydraulic-electronic systems [2].

Because of the need to introduce substantial amounts of scrap into the ingots, first-remelt furnaces are sometimes fitted with hoppers and batching devices. One of the batching mechanisms that has been developed takes the form of a drum with sixteen sections, which are filled with lump scrap. The sections are unloaded by turns through a hole in the bottom disk of the drum into a chute, through which the contents of each section slide into the crystallizer [2].

Furnaces of similar design can also be used to prepare (sinter) consumable electrodes from titanium sponge.

The selection of the types and deliveries of vacuum pumps used to service arc furnaces is determined by: a) the quantity of gases present in the material to be remelted; b) the optimum residual pressure in the furnace from the standpoint of supporting a stable arc; c) the maximum permissible residual pressure needed to prevent heavy absorption of gases by the consumable electrode and the liquid-metal pool.

As we noted previously, it is assumed as a guideline that 1 kg of titanium sponge contains 0.3-1.0 liter of gases. To meet the other two conditions, the residual furnace pressure should be held in the range from  $10^{-2}$  to  $10^{-3}$  mm Hg.

In calculating vacuum-pump capacity, it is also necessary to take account of leakage of outside air into the furnace and the liberation of gases from the deposits on the inner surface of the furnace (the computed vacuum-system capacity is usually increased by 40-50%).

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The permissible leakage is determined as a function of furnace dimensions: for large furnaces with crystallizer diameters of 500-800 mm, no more than 10 liters·μm/s of leakage can be permitted [2].

Since large amounts of gases may be liberated early in the melting process, vacuum-pump delivery must be increased as the residual pressure in the system rises. Two types of booster pumps - oil-vapor and mechanical - meet this requirement. Oil-vapor booster pumps perform successfully in the 0.01-0.1-mm Hg pressure range, and their characteristics do not depend on delivery pressure (up to 1-2 mm Hg). They are simple in design and have no moving parts. An important advantage of these pumps is the delivery increase that occurs when hydrogen is being pumped instead of air. The disadvantages of oil-vapor pumps include constant delivery at pressures above 0.01-0.1 mm Hg and their higher electric-power requirements. The Soviet industry has developed booster-pump designs delivering up to 15,000 liters/s [2, 32, 33].

In processes in which large amounts of gas are liberated at pressure of  $1.0 \cdot 10^{-2}$  mm Hg, it is most advantageous to use type DVN twin-rotor mechanical pumps. The rotors of such pumps revolve in the pump chamber without contacting one another or the casing walls. This makes it possible to drive them at high speeds (1-3 thousand rev/min), thus obtaining high delivery in a small-sized pump. Twin-rotor pumps also have other advantages - high efficiency, oil-free operation, a sealed casing that is shared with the motor, low sensitivity to dust and water vapor that enters the pump, and the ability to evacuate not only air, but also hydrogen. As compared with vapor-jet booster pumps, twin-rotor pumps perform in a higher pressure range, tolerate overloading, and thus deliver at higher rates. These pumps are used in sequence with forevacuum pumps. Since the pumped gases may contain substantial amounts of moisture, type VNG gas-ballast pumps should be used as forevacuum pumps. A separate gas-ballast pump is installed for preliminary evacuation of the furnace in some cases. Filters are inserted in the pipeline to the pump to

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protect it from dust that may be carried along by the air stream at the beginning of evacuation [2, 34].

The design of the filter should provide for replacement or switching of filtering elements under vacuum during operation of the furnace installation [35].

Steam-ejector pumps, which have a number of advantages over those hitherto used, have recently come into use for evacuation of metallurgical vacuum furnaces. For example, these pumps deliver at substantially higher rates than other pump types, have no moving parts, can transport dusty and corrosive gases, and deliver at higher rates as the entrance pressures rise. A six-stage pump can lower the residual pressure to  $10^{-2}$ - $10^{-3}$  mm Hg. A deficiency of the steam-ejector pump is the need for a steam source. Steam is used at a rate of 700 kg/h and condenser water at  $45 \text{ m}^3/\text{h}$  to pump at a rate of 10,000 liters/s; at 20,000 liters/s, the corresponding figures are 1000 kg/h and  $70 \text{ m}^3/\text{h}$  [33, 36].

Dynamolectric converters, such as the 85V, 6500A type GPN550-750 and the 40 V, 14,000 A type GPN560-375, are currently the preferred direct-current power sources for arc furnaces. These generators have efficiencies of about 85%.

Modern furnace installations are fitted with semiconductor rectifiers. Silicon rectifiers are preferred, since they survive heating better than germanium rectifiers, and this makes it possible to increase the specific current load carried by the rectifier. An investigation of a 5000-ampere silicon-diode rectifier showed that the arc burns quite stably despite the pulsating voltage supply that is characteristic for semiconductor rectifiers. The arc current and voltage follow the pulsations of the rectified voltage.

Modern arc furnaces are provided with devices for automatic control of melting. The unit used must support performance of a large number of operations, including: 1) striking the arc without short circuiting; 2) establishment of the desired arc length after the arc has been struck; 3) feeding the consumable electrode

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at the desired rate; 4) stabilization of the power dissipated in the discharge gap throughout the entire melting period; 5) quick correction of short circuits; 6) compensation of the resistance change of the consumable electrode that accompanied its depletion; 7) immediate lowering of the electrode in the event that a parasitic discharge arises or the arc is thrown to the crystallizer wall; 8) starting the furnace at reduced power (until the molten-metal pool has formed), switching to shrinkage-porosity extraction conditions, and switching off the furnace on completion of melting; 9) correction of the remelting electrical conditions when various types of charges are used.

A system that meets the above requirements and generally permits melting without intervention on the part of the smelter operator has been designed and is in the debugging stage [2, 37]. It has been reported that program-computer-controlled double-remelt arc furnaces have been placed in operation abroad [38].

Motion pictures made of an automatically controlled arc showed that its length varies only by a few millimeters in either direction, and that the arc voltage is constant to within  $\pm 0.25$  V [39]. Automatic control increased arc-furnace operating safety and the speed of the melting process. Double remelting of a 2-ton ingot required 4-5 hours [6, 26, 28, 39].

A unit using radioactive isotopes, such as  $\text{Co}^{60}$ , has been developed for continuous measurement of interelectrode distance. This level meter makes it possible to determine the molten-metal level in the crystallizer or hold it constant with an error of  $\pm 0.25$  mm [29, 40]. To improve safety and reliability of melting control, the furnaces are also equipped with remote systems for manual control of the process and direct observation of arc burning, using optical or television devices. Optical systems are currently regarded as more expedient, since they give a sharper and, which is very important, a color image.

A number of papers have considered the question as to the possible use of alternating current - single- and three-phase - in arc furnaces for smelting of titanium. The cost of the electrical equipment used in the furnace installation comes to about

30% of its total cost. Use of alternating current would lower the electrical-equipment costs by 1/3, or 10% of the total cost of the installation. Direct connection of high-power single-phase furnaces to the line one at a time cannot be permitted, since the phases would be unevenly loaded. In alternating-current work, cathode temperature is unstable because of the sinusoidal form of the current curve, especially at the times of zero passage, and this means a less stable arc. This applies in particular at a time when the arc is being struck. Alternating-current work requires a higher voltage than does dc, and this increases the danger of lateral arcing.

On direct current, about 2/3 of the power is dissipated at the anode, and use of the ingot as the anode increases pool depth. On alternating current, about 50% of the power would be dissipated in the ingot. Ingots smelted out with alternating current have comparatively poor surfaces. Attempts to eliminate these disadvantages of smelting titanium ingots with alternating current have been unsuccessful. When it is further taken into account that the efficiencies of semiconductor rectifiers are quite high, we might conclude that alternating current arc smelting of titanium is not highly promising.

#### Smelting in Electroslag Furnaces

The essentials of electroslag smelting are as follows: the joulean heat liberated in a slag as an alternating current passes through it heats the slag to 1900-2000°C, and this melts a consumable electrode immersed in the slag.

To prevent volatilization of the slag, an argon atmosphere is usually used for smelting. Before filling with argon, the furnace is evacuated to a residual pressure of 0.01-0.05 mm Hg. Figure 116 shows the design of an electroslag furnace [13, page 314; 41].

Alkaline-earth metal fluorides have been tested as fluxes for titanium smelting, and "pure" grade calcium fluoride has been found most suitable.

The electrical conductivity of a slag containing 87.3%  $\text{CaF}_2$  is  $5.5 \Omega^{-1} \cdot \text{cm}^{-1}$  at  $1700^\circ\text{C}$ . Conductivity rises with increasing  $\text{CaF}_2$  content in the slag [42].

A sealed hopper may be installed above the furnace to make up the slag losses incurred during smelting. The electroslag process can be used to melt titanium with large-section consumable electrodes or water-cooled nonconsumable electrodes. In the latter case, the titanium is introduced into the molten-metal pool in the form of sponge, lump scrap, etc. Below we present data on electroslag smelting of titanium ingots 90 mm in diameter with the two electrode types.

|                                     | Consumable electrode | Nonconsumable electrode |
|-------------------------------------|----------------------|-------------------------|
| Current, A                          | 2500-2700            | 1600                    |
| Voltage, V                          | 23-25                | 24-26                   |
| Electrode diameter, mm              | 60                   | 30                      |
| Slag-pool depth, mm                 | 25-30                | 25-30                   |
| Melting rate, kg/h                  | 40.5                 | 3.6                     |
| Specific power consumption, kW·h/kg | 1.6                  | 11.2                    |

We see from these data that nonconsumable-electrode smelting is inefficient.

Figure 116 shows that the electroslag furnace has much in common with arc-melting furnaces.

The peculiarities of the electroslag process can be used especially advantageously in electroslag furnaces for smelting heavy ingots - with weights exceeding 1-2 tons; the design is simplified and reliability is improved. A fundamental property of electroslag smelting - the absence of vacuum - requires the use of consumable electrodes with low hydrogen contents, since there is practically no reduction of hydrogen content as a result of electroslag smelting, in contrast to the case of vacuum-

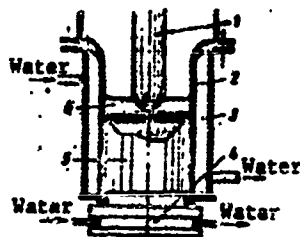


Figure 116. Schematic construction of electroslag furnace. 1) Consumable electrode; 2) crystallizer; 3) crystallizer cooling jacket; 4) bottom plate; 5) titanium ingot; 6) layer of molten slag.

are smelting. Since certain amounts of atmospheric moisture may be absorbed by the sponge during its production, grading, storage, and conversion into consumable electrodes, and by the finished electrodes themselves, electroslag smelting is used only to produce second-remelt ingots.

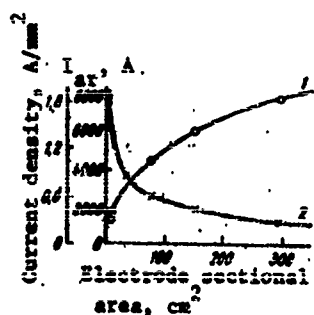


Figure 117. Optimum currents and current densities at consumable electrode during smelting of round titanium ingots by the electroslag process. 1) Current; 2) current density.

the same cross section for dc arc smelting are 0.10-0.15 A/mm<sup>2</sup>, i.e., approximately one-third as high.

The distance between the electrode and the crystallizer is determined by convenience in insertion of the electrodes into the furnace and may vary in a broad range - from 20 to 100 mm or more. An important advantage of electroslag smelting is the absence of the arc, which means that the separation between the electrode and the crystallizer need only exclude the possibility of short circuiting between them. The absence of metal spatter and the "crown" in the electroslag process and the uniform heating of the ingot by the slag over its entire surface even at clearances greater than 100 mm make possible thorough melting of the side surfaces of the ingot, so that it is sometimes unnecessary to rough it down before forming.

There are two current-flow possibilities in flux-shielded smelting: with the bottom plate insulated from the crystallizer,

Experiments in which ingots of titanium alloys such as OT4, OT4-1, etc. were smelted out by the electroslag process in a single remelting indicated that the hydrogen content in the ingots is within the permissible range if high-quality sponge is used.

The current needed for electroslag smelting is determined by the cross-sectional area of the electrode to be melted (Fig. 117). It is 0.3-0.4 A/mm<sup>2</sup> for electrodes with cross sections larger than 300 cm<sup>2</sup>. The

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all of the current from the consumable electrode flows through the slag pool to the ingot; when there is no insulation between the bottom plate and the crystallizer, the current may branch as it flows through the slag pool, part of it going through the liquid-metal pool to the ingot and bottom plate, and the rest through the crystallizer wall. As the fraction of the current flowing through the crystallizer wall increases, so does temperature in the electrode-crystallizer zone, i.e., temperatures are equalized throughout the entire volume of the slag pool, and this should have a favorable effect on the volume and shape of the metal pool.

As the power supplied to the furnace is increased, a larger percentage of the current flows to the crystallizer wall [43].

Installation of three electrodes in the furnace makes it possible to supply it with three-phase current. If all three are arranged in a row, it is possible to produce flat ingots, whose flat surfaces make it possible to send them directly to the forming stage.<sup>(6)</sup>

The specific electric power consumption in electroslag titanium smelting depends on smelting conditions, ingot size, and consumable-electrode dimensions. Low voltages - not above 26-30 V - are typical for the electroslag process. The specific electric power consumption came to 1.5-1.6 kW·h/kg in smelting ingots 120 mm in diameter with consumable electrodes 70 mm in diameter.

Thus, electroslag smelting of titanium has the following advantages: the possibility of dispensing with the dc source, smelting of large flat ingots, omission of the ingot-roughing and shrinkhole-extraction steps in many cases (because of the slag layer, which acts as heat insulation), and better operating safety because of the absence of the arc.

Experimental titanium and titanium-alloy melts were made with an electric arc under a layer of fused slag. The process was carried out at 60-70 V in an argon atmosphere at a pressure of 360-500 mm Hg. The increase in arc power increased the melting rate by a factor of about 1.5. The flux causes overheating

Footnote (6) is on page 559.

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of the surface layer of the molten-metal pool, warms the margins of the pool thoroughly, and produces an ingot with a quite even surface and no "crown." Flux smelting is by no means free of important disadvantages: dirtying of all parts of the furnace, including its vacuum elements, by flux dust and an increased explosion hazard [13, page 275].

#### Certain Problems of Operating Safety

Since titanium-smelting furnaces are potential explosion hazards, normal performance requires strict observance of safety rules that have been elaborated at the plants.

The safety measures to be observed in pressing electrodes reduce basically to removal of the explosive titanium dust from the zones in which it forms. The titanium sponge that sticks to the surface of the extrusion-die taper must be removed systematically, since otherwise the electrode will move through the die in jerks with the attendant dangerous waterhammer effects. A vacuum-cleaning system must be available to remove the dust and fine scale that form when the crystallizers are cleaned.

The basic danger that arises in vacuum arc smelting is burning through of the crystallizer walls by the electric arc. This allows water to penetrate into the furnace space and react with the molten or glowing metal with formation of hydrogen. However, hydrogen alone does not cause explosions. If, on the other hand, the wall tears or cracks as a result of the violent generation of steam and air penetrates through them, the result is a detonating gas that may explode and destroy the entire furnace. Water may be drawn into the furnace working space through cracks or open blisters in the crystallizer wall. Air may enter the furnace through the water-drain pipes.

Study of arc-furnace explosions has shown that they are not always caused by burning through of the crystallizer wall by stray lateral arcs. Inadequate delivery of water into the cooling jacket may intensify the generation of steam, with bursting of furnace elements as a consequence.

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Minute leaks sometimes form in the walls of water-cooled elements, and the entrance of water into the furnace may go unnoticed during operation of the pumping system. However, as the ingot cools with the vacuum system shut off, a substantial amount of hydrogen may accumulate in the furnace, and admission of air into it before it is opened may also produce an explosion.

Certain cooled furnace elements, such as the electrode-holder rod, the bottom plate, and the crystallizer, are also parts of the furnace power system and the voltage drops across them are significant. When the cooling water contains a certain quantity of salts, electric current passes through it between units that are at different potentials, and this is accompanied by solution of anode material. To eliminate this effect, elements in which substantial potential differences are possible must be electrically bonded, and softened water must be used for cooling.

Explosions may also be caused by oil from the vacuum pumps entering the furnace with the hot metal when the pumps are accidentally shut off, and by hydrocarbon vapor from rubber packings that decompose under the influence of local overheating.

Dusty titanium and magnesium deposits produced by condensation of their vapors during smelting on the cold crystallizer and vacuum-chamber surfaces can also form explosive mixtures with air.

The following basic measures are usually recommended for prevention of explosions in vacuum arc furnaces:

1. The arc length must be held as short as possible, no longer than the width of the gap between the electrode and the crystallizer wall. It is desirable to have the crystallizer wall thickness of the same order as the arc gap, i.e., about 40-50 mm. At this thickness, the length of the arc will increase as the wall melts, and this will shift it away before the wall has been burned through. One report [50] claims that a copper crystallizer 370 mm in diameter with a wall thickness of 40-45 mm was operated for several years without being burned through once. It is advantageous to make the crystallizers from seamless hollow shells fabricated especially for the purpose. Packings should be

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placed as far as possible from the zone in which the arc burns and protected with locally cooled heat shields. The requirements cited above pertain equally to the bottom plate.

2. The pressure of the gaseous phase in the crystallizer must be below the critical value conducive to glow-discharge formation. Practical experience has shown that explosions occur in furnaces operated at comparatively high residual pressures or in inert-gas atmospheres at pressures of a few millimeters of mercury.

3. The pressure in the furnace should be kept as low as possible in the event that water is sucked or forced into the furnace. This requires the use of vacuum pumps with high pumping speeds and delivery increasing with rising pressure in the pumped space.

As we noted above, twin-rotor pumps have such characteristics

If the delivery of the vacuum system is sufficient to remove all of the hydrogen and steam formed on entrance of water at comparatively low pressures (below 40 mm Hg according to [44]), the explosion hazard is sharply reduced. To prevent loss of vacuum and formation of explosive mixtures, vacuum furnaces are equipped with sensors that operate a quick-action vacuum slide to shut off the vacuum system when the pressure rises to a predetermined limit.

If the furnace pressure rises above atmospheric, the excess of gas is released through a safety valve adjusted to 0.1-0.3 atm. In this case, the excess pressure in the furnace prevents air from entering it. Explosion valves should be installed in pipe fittings situated as close as possible to crystallizer height. It is necessary to eliminate the possibility of air entering the furnace through the explosion valve.

4. The furnace must disconnect itself automatically from the electric power source when water enters it or when the water pressure in the main drops below the permissible norm. It is necessary to provide an emergency water supply that cuts in automatically. Check valves must be placed on the lines draining

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water from the main subassemblies (crystallizer, bottom plate, electrode holder) to eliminate the possibility of air induction into the furnace when the walls of the water-cooling system burn through.

5. The consumable electrode must be centered carefully on the axis of the crystallizer.

Consumable electrodes must be quite strong, since the arc is transferred instantly to the crystallizer when an electrode breaks off inside it.

6. When ingots are cooled with the vacuum pump off, i.e., in an inert-gas atmosphere, the gas must be pumped out of the furnace before the vacuum is broken.

7. The furnace may not be opened immediately in an emergency resulting from water, air, or vacuum oil in the furnace or melting of a gasket. The ingot must be allowed to cool completely and the furnace must be pumped out; only then may the furnace be opened with all precautions, since it may contain hydrogen.

The measures enumerated above do not completely eliminate the explosion hazard associated with smelting. For this reason, large industrial furnaces are installed in strong protective steel or reinforced-concrete bunkers. The bunker doors should be fitted with automatic interlocks that make it impossible to open them without shutting off furnace current.

Furnace control should be automated; the furnace should switch off automatically and sound an alarm on a departure from the predetermined conditions in any of its subassemblies. Furnaces are remote-controlled from a central desk equipped with a device for visual monitoring of the smelting operation [26, 45-47, 50].

Although electroslag furnaces, which have no arcs, obviously present less of an explosion hazard than arc furnaces, it is still possible for the crystallizer to burn through, for example when its cooling system malfunctions or the consumable electrode is short-circuited against the inner crystallizer wall. For this reason,

the above safety measures must also be observed in operating electroslag furnaces, including the erection of protective bunkers.

#### Prospects for the Development of New Furnace Designs

Although vacuum arc melting is used extensively in industry for titanium and its alloys, it is not free of serious deficiencies. Principal among these are the small size of the molten-metal pool, which makes it difficult to produce ingots with uniform chemical composition and structure, the difficulty of smelting out rectangular-section ingots, the explosion hazard presented by the furnaces, and the poor adaptability of arc furnaces to installations for production of titanium castings. It has been found that the difficulties of producing ingots of homogeneous composition and structure increase with increasing ingot weight. Although electroslag melting eliminates some of the disadvantages of arc melting, it does not solve all of the problems encountered in smelting titanium. For this reason, concurrently with improvement of the vacuum-arc and electroslag processes, research aimed at finding other smelting methods has been underway for a long time. Metal-liner smelting is a prime object of attention.<sup>(7)</sup> Since such furnaces are highly promising for smelting of titanium scrap, they will be discussed in Chapter 21.

Another trend is ordinary melting in induction-heated crucibles. The basic obstacle to this is the difficulty of finding a crucible material that will resist attack by the molten metal.

All these studies have a single objective: finding ways to increase the mass of the liquid-metal pool in order to make it possible to remelt lump titanium scrap and make castings from it.

Still another new melting process - the electron-beam process - is making rapid inroads into the industry. This method is characterized by the need for a high vacuum, of the order of  $10^{-4}$ - $10^{-5}$  mm Hg. The material to be melted is introduced into the furnace working space in the loose or compact solid form. When electron bombardment is used, the metal can be held in the molten state for a long time in a hard vacuum at temperatures substantially in excess of its melting point. Electron-beam melting

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makes it possible to solve a number of pressing technological problems: eliminate the preparation of consumable electrodes, smelt out complex-cross-section ingots, remelt scrap, and, with the appropriate monitoring facilities, eliminate smelter explosions.

Industrial electronic furnaces are rated at up to 1500 kW. As we should expect, electron-beam melting of titanium sponge does not lower the ingot's contents of impurity oxygen, nitrogen, iron, or carbon, but the hydrogen content is reduced from hundredths to ten-thousandths of a percent (by mass), with the result that specimens made from such ingots have shown impact strengths of 23.5-27.2 kgf·m/cm<sup>2</sup>, i.e., about one and a half times the figures for specimens produced by electric-arc smelting.

Electron-beam smelting of titanium alloys has produced similar results - a substantial drop in hydrogen content and a large increase in impact strength. Since melting occurs in a high vacuum, practically all of the manganese is removed from the titanium. It is therefore not advantageous to use the electron-beam furnace for titanium-manganese alloys.

The behavior of aluminum, which is used in most titanium alloys, in the electronic smelting process has been studied in some detail. It was found that the introduction of aluminum directly into the charge results in appreciable vaporization of the additive when it is present in amounts larger than 2.5%. No loss of tin occurred during electron-beam smelting of a titanium alloy with up to 3% of tin.

Thus, electron-beam smelting may be used to produce titanium alloys with many other elements - niobium, tantalum, vanadium, and others, as well as alloys with moderate aluminum and tin contents.

Although electron-beam smelting of titanium alloys does not increase their mechanical properties other than impact strength, the above advantages of this process may dictate its use for smelting of certain titanium alloys that are subject to more rigid requirements [49].

A radiation method has been proposed for smelting of titanium and titanium alloys.<sup>(8)</sup> Its essentials are as follows: a conical heater consisting of resistance elements made from graphite or high-melting metals such as tungsten or molybdenum is placed above a cooled crystallizer. The metal in the crystallizer is melted by radiation from the conical heater, whose temperature is brought up to 2600°C.

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Footnote (8) is on page 559.

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Footnotes

- | Manu-<br>script<br>Page<br>No. |   |
|--------------------------------|---|
| 517                            | <sup>1</sup> Patent (USA) No. 3,079,246, 1963.  |
| 523                            | <sup>2</sup> Patent (USA) No. 2,890,109, 1959.  |
| 536                            | <sup>3</sup> Patent (British) No. 758,024, 1957.  |
| 539                            | <sup>4</sup> See page 541.  |
| 542                            | <sup>5</sup> Miroshnikov, P.I. et al. Author's certificate (USSR),<br>No. 127,811.                            |
| 551                            | <sup>6</sup> Glazunov, S.G. et al. Author's certificate (USSR),<br>No. 130,184.                               |
| 556                            | <sup>7</sup> A process known earlier as smelting "in the floor,"<br>"in the shell," or "in the autocrucible." |
| 558                            | <sup>8</sup> Patent (USA) No. 3,075,263, 1963.  |

Symbol List

| Manu-<br>script<br>Page<br>No. | Russian | When<br>Typed | Meaning                 |
|--------------------------------|---------|---------------|-------------------------|
| 523                            | пот.э   | loss.e        | losses, electrode       |
| 523                            | пот.изл | loss.r        | losses, radiative       |
| 523                            | пот.исп | loss.e        | losses, evaporation     |
| 523                            | пот.т.п | loss.h.c      | losses, heat conduction |
| 523                            | пол.э   | u.e.          | useful eletrode         |
| 523                            | пол.сл  | u.i.          | useful, ingot           |
| 523                            | печи    | b             | furnace                 |
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## Chapter 21

### REFINING CERTIFIED TITANIUM AND TITANIUM- ALLOY SCRAP

#### General Information on the Process and Characterization of Scraps

Two basic kinds of scrap — certified and uncertified — are formed in the production of titanium sponge and titanium and titanium-alloy ingots and semifinished products.

Scrap contaminated with various impurities, chiefly at the surface of the metal, is usually referred to as certified scrap; it can be refined into commercial metal after removal of the superficial contaminants by various methods and subsequent re-melting of the metal. This section will consider the utilization of certified scrap, which includes chips, various trimmings, semifinished products with surface defects, ingot crowns, rejected pieces, etc.

Uncertified scrap is scrap in which the metal is contaminated not only at the surface, but also in volume; the extent of the contamination is greater, so that reclaiming the scrap requires application of such methods as electrolytic or thermal refining to purify the metal. Problems of reclaiming uncertified scrap will be examined in Chapter 25.

The problem of utilizing titanium and titanium-alloy scrap<sup>(1)</sup> is particularly pressing, and a great deal of attention has been

Footnote (1) is on page 598.

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devoted to it since the very beginning of industrial titanium production. As will be shown below, the relative amount of scrap formed when products are made from titanium is very large. In most cases, the titanium scrap is high-quality metal contaminated only at the surface by gaseous impurities. However, a number of difficulties stand in the way of utilization of titanium scrap.

Firstly, by far the greater part of the scrap is obtained in oxidized form, since titanium reacts with atmospheric oxygen on heating, which is an inevitable part of the process in which it is made; it also absorbs a certain amount of nitrogen in this process. Use of oxidized wastes in an ingot-smelting charge would lower the plastic properties of the metal in these ingots and lead to rejection of semifinished products.

Secondly, the preparation of consumable electrodes containing scrap, and especially lump scrap, would require a new technology for making the consumable electrodes and development of new titanium-smelting furnace designs in which the scrap is fed directly into the melting space. It would also be necessary to arrange for collection and storage of the scrap in such a way that it would not be declassified. It is not possible to use mixed scrap in titanium production in the same way as ferrous-metal scrap is used in the steel-smelting industry.

Thirdly, there was until very recently no efficient technology for processing titanium scrap into high-grade metal.

For a long time, the above difficulties remained insurmountable, with the result that titanium scrap went unused and accumulated at plant dumps or was used to cover subsidiary needs instead of the considerably cheaper nonmetallic titanium-containing materials. The result was highly unproductive waste of a valuable metal.

Discovery of ways to utilize titanium scrap would increase the reserves of the metal substantially and help lower the net cost of titanium semifinished and finished products. This last point is especially important for such an expensive metal as titanium, since its high cost is a substantial obstacle to wider

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application of this metal (see Chapter 1).

A number of published economic analyses have led American economists to the conclusion that extensive use of titanium in nonmilitary fields of engineering will be possible only if titanium semifinished products are made cost-competitive with stainless steel and nickel [51].

The economic advantage of utilizing titanium scrap in the ingot-smelting charge is obvious. Simple calculations indicate that even when a pilot-plant technology is used to prepare titanium scrap for smelting, the cost of the scrap is only a small fraction of the cost of sponge titanium.

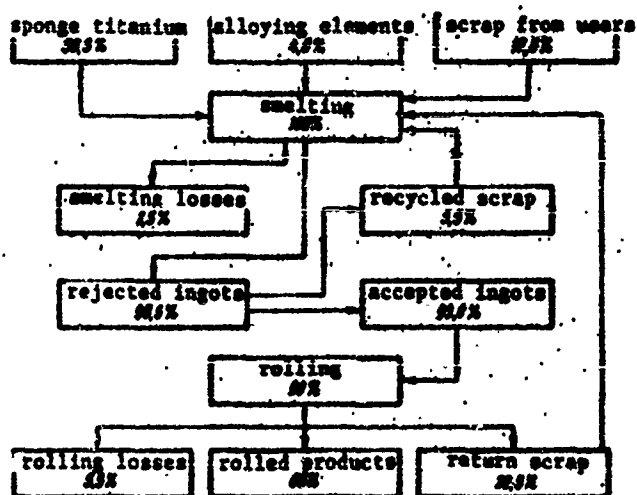


Figure 118. Chart of prospective technological process for smelting and rolling titanium at a large metallurgical plant.

Thus, in contrast to certain more common metals, the technology of utilizing scrap is one of the most important divisions of titanium metallurgy.

According to foreign publications, a number of firms and research organizations are engaged in work on the utilization of titanium scrap. Four years of work resulted in development of a method for grading unidentified titanium scrap originated by users [52].

The amount of scrap formed in the smelting and processing of titanium ingots depends on the level of the titanium-refining technology and the types of semifinished and finished products involved.

Figure 118 charts a projected technological process for the manufacture of titanium rolled products at a large mill using a thoroughly assimilated technology [53]. It follows from Fig. 118 that the yield of useful semifinished products represents about 65% of the charge. In reality, however, the yield of good ingots was until recently not 93%, as indicated in Fig. 118, but about 85%, and the useful yield in sheet production about 50% [54].

On the basis of available experience, it can be assumed that the yield of products from the ingot-smelting charge is 27% for pieces fabricated from sheet, 24% for pipes, and 18% for forgings; the irrecoverable losses are 5-10%. Consequently, about 70-75% of the metal used to smelt out ingots becomes scrap and is subject to regeneration [54, 55].

According to published reports, the firm Remkru (USA) uses about 25% of scrap in the titanium-smelting charge [56]. Another American firm, Titanium Metals (TMCA) uses arc furnaces at its Henderson plant to smelt out ingots weighing up to 3.4 tons from charges consisting 25-30% of scrap [57]. The British firm Imperial Chemical Industries (ICI) uses 40-50% scrap in smelting technical titanium and low alloys; the high alloys contain somewhat smaller amounts of scrap -- 30 to 40% [58].

The data of Table 40 [59-61, 139] characterize the average degree of utilization of secondary titanium in the USA; the table shows that the yearly average consumption of titanium scrap in the USA varies from 20 to 30% of the mass of the ingots produced. The lower scrap consumption in 1963-1966, which is paralleled by

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TABLE 40

Utilization of Scrap by the U.S. Titanium Industry in  
1957-1966

| indicator   | 1957  | 1958 | 1959 | 1960 | 1961 | 1962 | 1963  | 1964  | 1965  | 1966* |
|---|-------|------|------|------|------|------|-------|-------|-------|-------|
| titanium sponge production, tons                                | 15648 | 4160 | 3536 | 4818 | 6103 | 6105 | 7167  | 8200  | 8200  | 14500 |
| titanium sponge consumption, tons                               | 7548  | 3782 | 3598 | 4978 | 6351 | 6474 | 8042  | 10200 | 11000 | 18100 |
| production of titanium & titanium-alloy ingots, tons            | 9080  | 4600 | 5450 | 7327 | 8601 | 9438 | 10184 | 12700 | 13800 | 21300 |
| utilization of titanium scrap in smelting charge, tons          | 1501  | 1212 | 1532 | 2202 | 2260 | 2267 | 2112  | 2605  | 3000  | 4200  |
| ratio of amount of scrap to mass of sponge consumed, %          | 21.2  | 29.1 | 43.7 | 45.9 | 37.0 | 37.1 | 29.3  | 26.6  | 27.3  | 28.2  |
| ratio of amount of scrap utilized to mass of ingots produced, % | 17.6  | 24.7 | 28.1 | 30.4 | 26.7 | 24.4 | 20.9  | 20.5  | 21.8  | 19.7  |

\*Estimated

a marked increase in ingot casting, is apparently to be explained by increased production of high alloys, in which scrap is used in smaller amounts than in ordinary titanium alloys.

If we assume that 75% of the metal used in smelting out the ingots goes into scrap, the data of Table 40 and Fig. 118 indicate that the percentage of scrap returned to the charge for smelting of ingots in the USA during 1963-1966 represented 27% of the total amount of scrap formed.

Considering the high cost of titanium, a 27% degree of titanium-scrap utilization must be regarded as unsatisfactory. At the same time, secondary metals are used to produce about 50% of the steel, 40-45% of copper and copper-based alloys, 30-35% of aluminum alloys, and 25-30% of lead alloys.

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Utilization of technical titanium scrap has been partly responsible for the high quality attained in titanium sponge in recent years. To increase the hardness of the ingots, the British firm ICI even injects titanium dioxide into the smelting charge [62]. In the USA, up to 35% of oxidized scrap [63], apparently in the form of crushed shavings, is introduced into the charge instead of titanium dioxide.

As the quality of titanium sponge is improved, i.e., as its hardness is lowered, the amount of scrap that can be introduced into the smelting charge may reach 45% [137].

Metallurgical and metalworking plants produce an extremely wide variety of titanium scrap: chips, ingot "crowns," ingot templates, splices, rod and plate trimmings, sheet-cutting scrap, fins, broaching and punching scrap, butts, trimmings from hot- and cold-rolled sheets, odd pieces of sheets, rods, and other semifinished products, and, finally, various rods, sheets, finished workpieces, and the like that have been rejected for dimensional and other reasons, such as surface quality.

Experience has shown that it is most advantageous to classify scrap on the basis of the method used to inject it into the melt. All forms of scrap can then be broken down into two basic classes: chips, which go into the expendable electrode when it is pressed from titanium sponge, and lump scrap; the latter go into the consumable electrode or directly into the furnace at the first remelting of the ingot.

The above types of scrap are also differentiated in accordance with their degree of oxidation. For example, unoxidized chips and chips with various degrees of oxidation may be produced during processing of the same ingot or part. Thus there would obviously be no point in classifying the chips into two groups — oxidized and unoxidized — since this would complicate collection and storage. On the other hand, lump scrap must be sorted on the basis of the process stages in which it was formed (forging, pressing, etc.), to which the degrees of oxidation of the scrap also correspond. The procedure used to prepare this scrap for

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We noted above that titanium scrap is oxidized preferentially at the surface. Removal of this oxidized layer from the surface of the scrap by one method or another produces metal that is quite suitable for introduction into the charge for remelting. However, some scrap, chiefly chips from heavily oxidized ingots, billets, or forgings, may be saturated with oxygen through its entire cross section. Quite obviously, such scrap cannot be processed with a view to removing only the surface layer; it must be regenerated by some other method.

Two basic methods for the recovery of titanium scrap are used in the USSR and abroad: a) return to the melt after removal of the oxidized surface layer; b) electrolytic and thermal refining. The former method is applicable to surface-oxidized technical-titanium and titanium-alloy scrap, irrespective of form. Electrolytic and thermal refining of titanium presents independent problems that will be examined in Parts V and VII of the present volume.

Regeneration of scrap before remelting consists basically in removal of the oxidized surface layer. Electrolytic and thermal refining should be applied only to those types of scrap that cannot be sent for remelting, such as through-oxidized chips removed from ingots subjected to prolonged heating at high temperatures before pressworking, fine chips that have been contaminated with iron (screenings from degreased chips), pressroom scrap, the fragments of which usually include contaminants, unclassified scrap, such as chips and filings, obtained from customers, and scrap formed during dressing of primary titanium sponge.

Specialists estimate that about 70% of scrap can be sent for remelting after appropriate preparation; the remaining 30% must be refined.

Thus, figuring this time with finished rather than semi-finished products, we obtain the following tentative budget: metal in ingot-smelting charge 100%; finished product yield 15-25%;

certified scrap about 50%, uncertified scrap to be refined electrolytically or by other methods about 20%, and irrecoverable losses 8-12%.

The question as to the maximum permissible content of scrap<sup>(2)</sup> in the ingot-smelting charge is of prime importance. Obviously, a substantial amount of scrap must be remelted repeatedly if the useful product yield is 15-25%. As we noted earlier (see page 530), remelting of titanium is, in itself, of little detriment to the quality of the metal.

In practice, however, a strength increase of approximately 3-5 kgf/mm<sup>2</sup> is nevertheless observed when titanium is remelted in industrial furnaces; this corresponds approximately to a 0.04% increase in the metal's oxygen content. Thus, scrap returned for melting after removal of the oxidized surface layer will contain progressively larger amounts of oxygen distributed uniformly over the entire cross section of the secondary-metal lump, with the result that the percentage of scrap introduced into the charge must be limited to keep the total oxygen content in the ingot below a definite limit. Another factor that must be considered in determining this percentage is that the oxygen present in the surface layers of the scrap may not be removed completely by surface processing of the scrap.

S.I. Sychevoy and G.D. Zyukov-Batyrev [13, page 282] proposed a formula that can be used to calculate the maximum amount of scrap that can be introduced into an ingot-smelting charge:

$$C = C_r + \frac{100}{100-N} \Delta C_r + \frac{N}{100-N} \Delta C_s \quad (1)$$

where C is the maximum permissible oxygen content in the ingot smelted out, in %; C<sub>s</sub> is the average oxygen content in the titanium sponge, in %; ΔC<sub>r</sub> is the increase in ingot oxygen content caused by arc-furnace remelting, in %; ΔC<sub>s</sub> is the oxygen-content increase in the scrap due to incomplete removal of the oxygen-enriched surface layer from the scrap, in %; and N is the percentage of scrap that can be introduced into the ingot-smelting charge, in %.

Footnote (2) is on page 598.

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According to the prevailing Soviet and foreign technical specifications for titanium and titanium-alloy ingots, oxygen content may not exceed 0.2%. Titanium sponge usually contains no more than 0.1% of  $O_2$ . The increase in oxygen content during smelting may, as we noted above, be assumed equal to 0.04%. Substituting these values into the above equation, we can determine the permissible scrap oxygen concentration resulting from oxidation of the surface layers of the scrap for various scrap percentages returned to the charge for melting.

The calculated results may be expressed as follows:

| Percentage of scrap recycled                                  | 10    | 20    | 30    | 40    | 50    | 60 |
|---|-------|-------|-------|-------|-------|----|
| Permissible oxygen concentration in scrap ( $\Delta C_s$ ), % | 0.055 | 0.050 | 0.043 | 0.033 | 0.020 | 0  |

We see on examination of these data that under the existing requirements defining oxygen concentration in titanium alloys, and at the prevailing titanium-sponge oxygen concentration, the permissible oxygen content in scrap resulting from surface oxidation is rather low and diminishes rapidly with increasing percentage of scrap introduced into the smelting charge. For example, use of 60% of certified scrap in the charge would be possible only if the scrap had no oxygen impurity at all, which is unrealistic. It follows from the data of S.I. Sphevoy and G.D. Zyukov-Batyrev that up to 50% scrap can be introduced into the charge for smelting out titanium and titanium-alloy ingots at the present time, i.e., all of the certified scrap can be used (see the scrap balance sheet presented above)

Thus, the combination of remelting and refining of scrap permits efficient use of all titanium scrap generated at both the metallurgical plants and by consumers, i.e., at metalworking plants. Although the amount of chips removed from titanium ingots in the roughing process is decreasing steadily as the smelting technology is improved, the relative quantity of chips in scrap formed at metalworking plants that produce finished products from semifinished titanium products is considerable. It can be

assumed in approximation that chips make up 30-40% of the total quantity of titanium scrap.

For practical purposes, compact titanium oxidizer at temperatures above 550-650°C. However, ingots and semifinished products are heated several times to 950-1200°C for comparatively short periods in oil-fired or electric furnaces without protective atmospheres before they are pressworked. During this process, two oxygen-saturated layers — scale and the deeper-lying so-called alphas layer — form on the surfaces of the ingots and, consequently, on the scrap obtained from them. The scale is composed for the most part of titanium dioxide (rutile) [64], so that its oxygen concentration is near 40%. The scale is usually weakly bonded to the metal and can be removed from it mechanically. The alphas layer is a superficial oxygen-enriched layer of metal. Its oxygen content diminishes with increasing depth. American investigators take the distance at which the hardness of the metal has increased by 75 Brinell units as the depth of the alphas layer.

The depth of oxygen penetration into cylindrical specimens of technical titanium and the alloys Ti-4Al-4Mn and Ti-5Al-2.5Sn has been determined by microhardness measurements [65]. During 1 hour at 980°C, oxygen penetrates to a depth of 0.25 mm into technical titanium, to 0.2 mm into the alloy Ti-4Al-4Mn, and to 0.1 mm into Ti-5Al-2.5Sn.

Reference [66] submits the following equation for the depth of oxygen penetration into the alloy Ti-5Al-2.5Sn in the 315-760°C range (as a function of holding time):

$$X = 4.13 + 0.5 \lg t - \frac{8430}{T}, \quad (2)$$

where X is the layer thickness in mm corresponding to a 75-unit increase in Brinell hardness; t is the time in hours; T is the holding temperature in °K.

The values of X calculated from the data of [65] and [66] agree.

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It has been established that forging scrap is most heavily oxidized; its surface carries a relatively thick layer of scale and, beneath that, an alphasized layer whose depth may range from 0.6 to 2 mm or more in various alloys, depending on heating time and temperature. Under hot working, some of the scale is discarded with the scrap, but the rest of it is pressed into the surface layer of the metal, forming oxygen-enriched zones.

Pressroom scrap is only lightly scaled, and the alphasized-layer depth does not usually exceed 0.5 mm. In some cases, however, this scrap is contaminated with various lubricants used in pressworking.

Very little scale is found on scrap from rolling (including sheet-rolling) production, and the depth of the alphasized layer is no more than 0.1-0.2 mm. However, this scrap has a comparatively large specific surface area, and the oxygen-concentration increase resulting from surface-layer oxidation may therefore be quite large.

Chips have even larger specific surface areas. Even an insignificant amount of surface oxidation (the appearance of temper colors) may result in a substantial increase in the oxygen concentration in the chips. Moreover, chips produced during machining of forgings and other heavily surface-oxidized workpieces may consist entirely of alphasized metal and have extremely high oxygen concentrations even in the absence of temper colors. However, most of the chips are usually formed on removal of deeper layers of metal rather than the surface layers.

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Titanium alloys are less plastic than alloys based on iron and nickel. As a result, less heat is generated during cutting of titanium. However, the average temperature in the deformed zone is higher for titanium because of its lower thermal conductivity. Other conditions the same, cutting temperatures were as follows at a cutting speed of 600 m/min: 1500°C for titanium, 1300°C for stainless steel, and 800°C for ordinary steel [67]. Thus, conditions promoting oxidation of the chips are created during cutting of titanium.

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However, the chips do not oxidize at temperatures below 300°C. A tool-cooling cutting fluid was tested as a means to reduce chip oxidation. This did in fact produce an unoxidized chip, but the subsequent operation of degreasing was greatly complicated [68]. Chip oxidation can be prevented completely or in part by feeding gaseous CO<sub>2</sub> at 0-2°C into the cutting zone [69]. If the chips do not oxidize at temperatures below 300°C, this temperature could evidently be maintained by feeding compressed air into the cutting zone; this would be much cheaper and simpler than the use of carbon dioxide.

Below we present oxygen contents in the superficial alphized layers of scrap from various alloys and the depth of this layer after heating of large-section workpieces for forging and stamping [13, page 282].

|   | VT1 | OT4 | VTZ-1 | VT5 | VT6 | VT8<br>(cast) |
|---|-----|-----|-------|-----|-----|---------------|
| Oxygen-content increase<br>in alphized layer,<br>mg/cm <sup>2</sup> | 2.8 | 1.5 | 2.5   | 4.2 | 2.2 | 7.3           |
| Total depth of alphized<br>layer, mm                                | 0.8 | 0.2 | 0.6   | 2.0 | 0.6 | 0.5           |

A calculation based on the above data indicates that, for example, block-shaped forging scrap weighing 5 kg or sheet cuttings of technical titanium 1 mm thick cannot be introduced into the ingot-smelting charge in substantial amounts without preliminary removal of the alphized layers.

#### Collection of Scrap and its Preparation for Refining

Titanium chips can be classified into two types on the basis of degree of oxidation: a) slightly oxidized silvery scrap (containing less than 0.2% O<sub>2</sub>), b) yellow oxidized scrap (containing 0.20-0.30% O<sub>2</sub>), and c) heavily oxidized brown scrap with bluing (containing 0.3-0.6% O<sub>2</sub>).

As compared with the initial metal, chips are also richer in iron, aluminum, silicon, and carbon. The higher contents of the first three elements in the chips result from its contamination during collection and storage. Carbon enters the chips when cutting emulsions are used and when the chips are contaminated by

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oils. In addition, the chips may contain fragments from the carbide tools used to machine the metal. The chips are magnetically separated to remove them. So that the cutting-tool fragments will have magnetic properties, titanium ingots must be cut with hard-alloy tools containing at least 6% Co. Magnetic separation also removes the iron, some of which is acquired as a result of cutting-tool wear. Hydraulic jiggling is also used to remove fragments of carbide cutting tools from titanium chips. Tool fragments settle to the bottom of a water-filled conical separator through which air is passed; the substantially lighter titanium chips accumulate at the top of the separator [142]. Other mechanical impurities can be removed by appropriate cleaning of the chips prior to etching.

Since most titanium chips are produced at the titanium-using plants, it is very important to prevent intermixing of chips from different titanium alloys and mixing of these chips with chips of other metals. This is accomplished by taking appropriate organizational-technical measures.

The bulk weight of curled titanium chips is about  $0.1 \text{ kg/dm}^3$ , which precludes processing it in uncrushed form. The size limit of crushed chips is determined by the technology of its subsequent utilization. If it is loaded directly into arc-furnace hoppers, the chip fragments may not exceed 50-70 mm in length. Chips introduced into charges from which consumable electrodes are to be pressed may have lengths up to 100 mm.

Tests of jaw crushers and vibration and ball mills under production conditions indicated that they are unsuitable for grinding titanium chips. Fine chips, no larger than 40 mm, are obtained from the hammer mill. However, this overheats the chips, so that there is a certain amount of additional oxidation.

The conventional conical chip crusher, which produces chips less than 50 mm in length, is most suitable for crushing chips that are to be used in making consumable electrodes. The bulk weight of the crushed chips is  $0.5-0.6 \text{ kg/dm}^3$ .

Chips are always more or less contaminated by oil even when they are formed without the use of a cutting fluid. The dirty chips are washed in a tank with hot running water at 80-90°C and then dried in hot-blast driers at temperatures no higher than 200°C.

Heavily contaminated chips can be degreased in carbon tetrachloride, which, unlike other organic solvents such as gasoline or dichloroethane, is noninflammable.

The foreign literature recommends tetrachloroethylene for degreasing of metals. Its vapor (boiling point 121°C) is fed into a chamber filled with the material to be cleaned. Condensing on its cold surfaces, the tetrachloroethylene washes all contaminants from them [70]. In many cases, it is sufficient to wash the chips with hot water or treat them with live steam.

After degreasing and drying, the chips are passed through a magnetic separator and then screened. The screenings represent a few percent of the initial mass of the chips. They can be sent for electrolytic refining or used to make ferrotitanium master alloys.

Preparation of lump scrap begins with grinding to dimensions determined by the technology of subsequent utilization. The lumps of metal are usually forged into large billets about 40-50 mm in diameter and cut into lengths of about 150 mm or torch-cut into fragments of arbitrary shape.

Tests of various methods of cutting titanium have shown that it is most advantageous to use an automatically fed and lubricated band saw with 24 teeth per decimeter. The speed of the saw is about 30 m/min and the feed 13-20 mm/min [71].

A comparison of methods used in cutting large pieces of titanium scrap — mechanical and oxyacetylene — has shown that on the basis of labor cost and wastage of metal, oxyacetylene cutting is used to advantage when the fragments are not excessively large. Mechanical cutting is superior for large pieces of scrap, such as rods more than 50 mm in diameter [72].

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Oxyacetylene cutting of scrap is a simple and productive operation. Although the surface of the cut is severely oxidized, the alphasized layer at this surface is comparatively shallow because of the high cutting speed. The zone of the cut must be removed by machining or some other method.

From the standpoint of cutting speed and, consequently, deduced thickness of the alphasized layer that is formed, oxygen cutting of titanium appears to merit attention. In this method, the cut is begun with an ordinary flame and then, when the metal in the cutting zone has been heated to high temperature, only oxygen is fed into the torch. Cutting is supported by the heat of the exothermic titanium oxidation reaction. Sheets of technical titanium and the alloy Ti-6Al-4V 5 mm thick could be cut at 4 m/min, with cut widths less than 1 mm [73]. Experiments in the plasma cutting of titanium have been started.

Titanium can be cut with a friction saw, whose disk should be made from a steel that does not temper [74].

Each fragment of scrap is stamped to indicate the type of alloy. Scrap grades are controlled by qualitative spectral analysis in which the chemical composition of the metal fragment is determined with a steelscope. However, quick and dependable determination of impurity and especially gas contents in scrap is a still unsolved problem. Obviously, indirect methods, such as hardness determination, are not suitable for routine quality-control of scrap. Determination of gaseous-impurity content by spectral analysis appears to be most convenient. Appropriate methods should be developed for this purpose.

The quality of chips and small sheet cuttings is evaluated by taking an averaged sample from the consignment and melting it into an ingot for subsequent analysis. However, this method is excessively slow, complicated, and little suited for large-scale routine analyses.

Attempts are being made to evaluate scrap quality indirectly by statistical calculations based on the increase in the ultimate strength of ingots smelted using scrap of a given grade and form

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that has been prepared for melting by a certain method. It may be expected that the use of theoretical coefficients obtained in this way will make it possible to use certain forms of scrap in the charge without quality control and still obtain alloys with mechanical properties that conform to the technical specifications in point.

Another problem that still has no practical solution is that of finding ways to enable plants that smelt titanium and titanium-alloy ingots to recycle their own scrap. Utilization of scrap generated at metal cutting plants is more complex. A draft classification of titanium debris and industrial scrap was elaborated during the preparation of a State Standard for titanium and titanium-alloy scrap. According to the prevailing technical specifications, grade 1 scrap can be returned to the melt after degreasing and removal of mechanical contaminants, while scale and the alphasized layer must be removed from grade 2 scrap before recharging [13, page 282].

Oxidized chips and uncertified scrap are sometimes used instead of ferrotitanium in ferrous metallurgy, but this is irrational. Ferrotitanium can be prepared by other, cheaper methods, while titanium scrap can be regenerated electrolytically. About 60% of the titanium is burned off when titanium scrap is used in ferrous metallurgy [75]. Obviously, organization of ferrotitanium melting from unregenerated uncertified scrap directly at the plants producing titanium semifinished products would make it possible to utilize this scrap with incomparably greater effectiveness.

As we have noted, the scale layer on titanium and titanium alloys is weakly bonded to the surface of the metal. In view of this, it was proposed immediately after the organization of industrial titanium production that the scale be removed mechanically from titanium ingots and semifinished products. Mastery of such methods was of substantial interest, since the scale formed on titanium at temperatures above 700-750°C is insoluble in most etchants used on titanium.

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Sand-blasting is used in the USA to clean hot- and cold-rolled annealed titanium strip. Sand consisting of particles about 0.4 mm in diameter is used for this purpose; it is blasted with a stream of air under a pressure of about 8 kgf/mm<sup>2</sup> [76]. Sand blasting causes minute SiO<sub>2</sub> particles to penetrate into the surface layer of the metal to be cleaned, but this layer is removed on subsequent etching.

Since the use of dry sand-blasting machines is prohibited in the USSR owing to the harmful effects of the process on health, wet-sand and shot-peening methods have been tested for cleaning lump titanium scrap. Wet-sand cleaning was found to be less efficient than shot-blasting and requires use of cumbersome equipment for regeneration of the sand. Later experiments therefore made use of a rotary-table shot slinger with the following characteristics: chilled iron shot 0.2-3 mm in diameter, rotor speed 2450 rev/min, shot velocity 80 m/sec at feed rate of 130 kg/min, width of shot cone at nozzle 60 mm.

The experiments showed that the scale can easily be removed from lump scrap by this method; it is also possible to take part of the alphasized layer with it.

Plates 3-5 mm thick with surface areas from 50 to 100 cm<sup>2</sup> were used to determine the weight loss from 1 cm<sup>2</sup> of surface by specimens of OT4, VT3-1, and VT5 alloys that were processed in this unit. The OT4 specimens had an oxidized surface after hot rolling and had been held for 1 hour at 950°C. The plates of VT3-1 alloy were heated by ordinary forging, followed by planing and holding for 1 hour in an electric furnace at 1150°C. The loose part of the scale was removed from the plates of OT4 and VT5 alloys prior to the shot-slinger treatment. The test results appear in Table 41.

As calculated from the resulting data, the depth of the layer removed by shot slinging comes to about 0.07 mm for specimens of OT4 alloy (with an alphasized-layer depth of about 0.15 mm), also about 0.07 mm for the specimens of alloy VT3-1 (alphasized layer about 0.36 mm), and about 0.11 mm for VT5 (alphasized layer

TABLE 41  
Weight Loss of Titanium-Alloy Specimens as Function of  
Process Time in Shot Slinger

| alloy | specific specimen mass loss, g/cm <sup>2</sup> ,<br>after treatment for various times, min. |       |       |      |       |      |
|-------|---|-------|-------|------|-------|------|
|       | 5   | 10    | 15    | 20   | 25    | 30   |
| OT4   | 0.02  | 0.025 | 0.03  | 0.03 | 0.03  | 0.03 |
| VT3-1 | —   | 0.01  | 0.01  | 0.02 | 0.025 | 0.02 |
| VT5   | —   | 0.025 | 0.025 | 0.03 | 0.04  | 0.03 |

about 1.75 mm). It appears that shot slinging removes only the superficial part of the alphas layer, which is most heavily saturated with oxygen and, consequently, brittle. The deeper, softer part of this layer is probably only cold-hardened by the shot.

Use of iron shot increases the iron content in the surface layers of the scrap fragments processed. For example, it rose from 0.15 to 0.19% in the case of OT4 alloy. The experiments indicated that the iron-containing surface layer is removed during subsequent etching.

A rotating-drum shot slinger should be used to process lump titanium scrap. Tumbling also removes scale from lump titanium scrap [13, page 282; 66]. The lumps of scrap themselves act as shot. The tumbling operation is considerably less productive than shot slinging. However, it does not require complicated equipment.

The time required to clean scrap in the tumbling drum depends on the speed at which it rotates and the level to which it is filled. Observations indicate that tumbling cleans the surfaces of the scrap mainly as a result of friction of one fragment against another rather than by knocking them together. In virtue of the simplicity and low cost of the tumbling machines and the fact that it is unnecessary to watch them constantly, these devices are coming into use on a steadily increasing scale [13, page 282].

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If necessary, cuttings from hot-rolled products are etched, followed by cutting with guillotine shears to obtain pieces of the size required for introduction into the consumable-electrode charge. The cut trimmings are degreased.

Trimmings from rolled sheet and ribbon are generated when the etched sheet material is culled. As a rule, these trimmings do not require further etching, and are only degreased. Lump titanium scrap is usually not degreased.

It has been suggested<sup>(3)</sup> that sheet titanium scrap be cut with a toothed blade. The resulting strips are then bent into incomplete rings, which interlock with one another and fragments of sponge during subsequent pressing of the consumable electrode. As a result, the mechanical strength of the electrode — by comparison with an electrode made from sponge alone — is lowered to a substantially lesser degree than when flat cuttings are introduced into the consumable electrode.

The bending angle of the strips depends on their width when sheet scrap 0.6-2.0 mm thick is cut: it is 145° at a width of 7 mm and 320° at a width of 2.4 mm. The minimum permissible strength of the consumable electrode is reached when 30% of ordinary sheet trimmings are introduced into it. Use of the ring-shaped trimmings makes it possible to increase the trimming content in the electrode to 50%.

#### Etching of Scrap

Many etchants have been suggested for cleaning the surfaces of titanium and titanium-alloy semifinished products. Those used in practice can be broken down into three main groups: aqueous etchants, melts, and compositions for electrolytic etching.

As we know, titanium dioxide is soluble with difficulty in acids and alkalis. Preliminary removal of the dioxide from the surface of the scrap by shot slinging or tumbling makes it much easier to dissolve the aliphized layer.

We noted in Chapter 1 that titanium is not stable in hydrofluoric, phosphoric, and certain other acids. Thus, most acid etchants include hydrofluoric acid or a fluoride, which are the

Footnote (3) is on page 598.

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most readily available and cheapest materials as compared with the other acids named above. Use of fluorides is cheaper and more convenient than use of the acid itself.

The influence of oxygen dissolved in the titanium on etching rate is extremely important. It was established in [77] that titanium with a low oxygen content (up to 0.5% O<sub>2</sub>) dissolves faster in 6% HF solution than titanium containing 1% O<sub>2</sub> in 12% HF solution. This report is confirmed by [78] and by practical data.

Since it is usually necessary to cut lump scrap with an acetylene torch, the cut surface is found to be oxidized. It has been established experimentally that this oxide layer does not come off in aqueous etchants. Since chips are not as heavily oxidized, aqueous etchants can be specified for them. However, the same etchant — pyrophosphoric acid — was originally used for both lump scrap and chips in order to standardize etchant compositions [68].

To obtain the pyrophosphoric acid, grade 1 technical orthophosphoric acid (70% solution) was heated until boiling stopped; this occurs at about 200°C. At this point, most of the orthophosphoric acid has been converted to pyrophosphoric. Etching in pure pyrophosphoric acid, whose preparation involves certain difficulties, showed no advantages over etching with a mixture of these acids.<sup>(4)</sup>

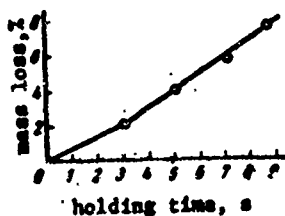


Figure 119. Mass loss of titanium chips during etching in pyrophosphoric acid at 220-240°C.

Figure 119 shows the mass loss of titanium chips during etching in pyrophosphoric acid at 220-240°C as a function of etching time. It was established that the minimum oxygen content in the etched chips is reached at a 2% mass loss. To minimize the phosphate content in the etched chips, they must be washed thoroughly after etching in hot 3% HCl solution and then in water.

Footnote (4) is on page 598.

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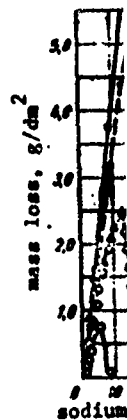


Figure 12 of metal hydrochloric acid fluctuations (S. Ye.V. Kor Yevseyevs  
2) 35% HCl  
4) 7.0% HCl

Large pieces of scrap -- "crowns" and templates -- were also etched in pyrophosphoric acid. Since they are of the same diameter as the ingot, they were cut into pieces with an acetylene torch. The surface of the cut was cleaned by sand blasting for 10 minutes at an air pressure of 6 atmosphere, and the scrap fragments were then etched in pyrophosphoric acid for 20-40 minutes at 220-240°C, followed by washing and drying in the same way as the chips. The "crowns" were not sand-blasted.

After pyrophosphoric-acid etching, chips and fragment scrap acquire a characteristic silvery luster.

Pyrophosphoric acid was used to etch titanium scrap on an industrial scale. Up to 30% of chips or up to 50% of lump scrap was introduced into the consumable electrodes after pyrophosphoric-acid treatment.

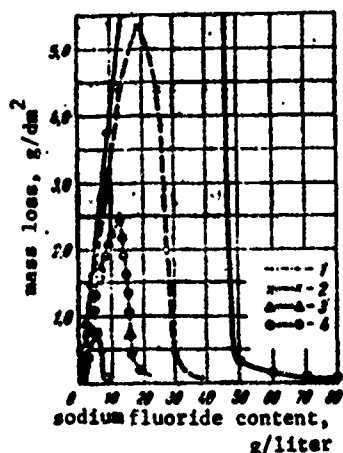


Figure 120. Etching losses of metal as functions of hydrochloric acid and sodium fluoride concentrations (S.A. Kushakevich, Ye.V. Konstantinova, Z.K. Yevseyeva). 1) 70% HCl; 2) 35% HCl; 3) 17.5% HCl; 4) 7.0% HCl.

An advantage of pyrophosphoric acid is its high activity, which enables it to remove the densest oxide crusts from the titanium surface. However, this acid also has substantial disadvantages as an etchant. Chip etching requires only a few seconds, and the chips are often overetched under industrial conditions and take up considerable amounts of hydrogen. Substantial amounts of acid are required to etch large pieces of scrap, and this increases the cost of the etching operation markedly at the high cost of the acid.

Numerous investigators have studied the etching of titanium semifinished products that have been held in the 800-1000°C temperature range for certain spans

of time. Solutions of mineral acids — HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> — with fluoride additives — CaF<sub>2</sub>, NaF [1, page 276; 79] — were used as etchants. It was found in tests of an etchant consisting of HCl and NaF that etchant activity is determined not only by hydrochloric acid content, but also by the NaF content, and that a certain NaF content at which the etching effect is maximized corresponds to each HCl concentration. A further increase in the NaF concentration reduces the solubility of the metal as a result of formation of a protective film on it (Fig. 120). This makes it possible to lower the HCl concentration without detriment to the etchant effect.

It was found in [78] that turbulizing with air lowers the etching rate, and to a greater degree than does the similar use of nitrogen. The cause of this phenomenon was ascertained in [80], which demonstrated that the corrosion of titanium is inhibited substantially as the concentration of Ti<sup>4+</sup> ions increases in the solution. Ti<sup>3+</sup> ions are formed when titanium is etched in acids; however, if Ti<sup>2+</sup> ions are formed, they are quickly transformed to Ti<sup>3+</sup> if the solution contains an oxidizing agent, such as dissolved oxygen. Ti<sup>3+</sup> ions are oxidized to Ti<sup>4+</sup> comparatively slowly.

Thus, turbulizing of the etching solution with air should promote the oxidation of Ti<sup>3+</sup> to Ti<sup>4+</sup>, i.e., lower the etching rate; this has been confirmed by practical data. The implication is that the etching solution should not be turbulized, but should be depleted in the shortest possible time.

A shortcoming of etchants containing H<sub>2</sub>SO<sub>4</sub> and CaF<sub>2</sub> consists in the low solubility (0.6%) of the CaF<sub>2</sub> in the acid, as a result of which most of the CaF<sub>2</sub> remains in the solid phase. As etching progresses, the amount of this phase does not decrease, since the CaSO<sub>4</sub> that is formed also has a low solubility.

Reference [68] examined the possibility of etching scrap in a solution containing 12% HCl and 5% NaF, which can be used to treat titanium semifinished products. The mass loss came to 1.5% when titanium chips were etched at room temperature for 0.5 min.

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The same mass loss is reached in 3 minutes in a less concentrated etchant — 5% HCl and 2% NaF.

An etchant consisting of hydrochloric acid and NaF does not etch oxidized lump scrap. In pilot-plant tests of this etchant, chips were loaded into a copper basket in 10-15-kg batches and etched in a rubberized tank at room temperature. The etching time required for the first batches of chips was 2 minutes; it then increased to 3 minutes and reached 5 minutes by the end of the process.

The mass loss of the chips during etching under industrial conditions was 4-6%. Attempts to lower this figure were unsuccessful, since some of the chips remained unetched when the etching time was shortened.

An etchant consisting of sulfuric acid and sodium fluoride was used successfully to etch tumbled lump scrap and chips.

When etchants containing the fluoride ion are used, it is necessary to detoxify the spent solutions to reduce their fluorine concentration to 1.5 mg/liter.

A number of melts whose principal component is sodium hydroxide have been proposed as etchants. They incorporate additives that inhibit hydrogenation of the titanium:  $\text{NaH}_2$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{CO}_3$  [66, 81-83]. Use of a mixture of NaOH and KOH to lower etching temperature was suggested in [84], although it would appear that this would increase the cost of the etchant. Alkali baths remove only the oxide layer and do not affect the alphas layer.

The high process temperature (at least 350-400°C) requires heating of the etching baths and may result in ignition of the material being processed; it also complicates the etching units and makes them more expensive to operate.

However, development of an etchant consisting of potassium salts with inhibitor additives has been reported; its working temperature is 200-220°C. It removes scale from semifinished titanium products rolled or annealed at temperatures up to 1040°C. Titanium treated in this etchant undergoes practically no hydrogenation [138].

Many investigators, including the author of [85], have made detailed studies of the absorption of hydrogen by titanium.

It is assumed that hydrogen diffuses into titanium in the atomic form. At 20°C, the solubility of hydrogen is 0.002% in  $\alpha$ -titanium and 0.0066% in  $\beta$ -titanium. Not only the solubility, but also the diffusion coefficient of hydrogen increases with rising temperature;  $\alpha$ -titanium absorbs hydrogen more slowly than  $\beta$ -titanium. In alloys containing  $\beta$ -Ti, hydrogen diffuses rapidly into the interior of the specimen.

It has been found by x-ray structural analysis [86] that brief etching of titanium at room temperature results in formation of the coarse-grained titanium hydride TiH. Prolonged exposure to the acid results in formation of the fine-grained hydride TiH<sub>2</sub>. Both hydrides have the face-centered cubic lattice;  $a = 4.38 \text{ \AA}$  for TiH and  $a = 4.46 \text{ \AA}$  for TiH<sub>2</sub>.

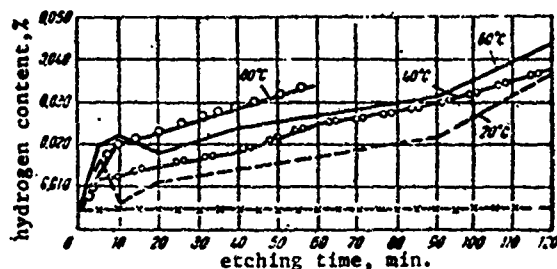


Figure 121. Variation of hydrogen content on surface of VT1 titanium sheets as a function of etching time and temperature in solution of hydrochloric acid and sodium fluoride (S.A. Kushakevich, T.V. Shikhaleyeva). x - x) analysis of (thickness) centers of specimens at the same temperatures.

When titanium is placed in the acid, the superficial oxide film dissolves first, and then the titanium; some of the hydrogen evolved is assimilated by the titanium with formation of the hydride. Subsequently, the newly formed hydride and the metal dissolve simultaneously; equilibrium is established between the

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rate of hydride formation and the rate of its solution, with the result that the hydride film grows to a certain thickness, which then remains constant [87].

S.A. Kushakevich and T.V. Shikhaleyeva [1, page 276] reported that the hydrogen concentrates in a thin surface layer (0.01-0.02 mm) during etching; its content here is about 5 times the content deep in the metal, where it remains unchanged even after very long etching (Fig. 121).

The amount of hydrogen absorbed during etching of titanium alloys depends on the amount of the  $\beta$ -phase, the size and shape of its grains, and the activity of the etching process. Although appropriate thermochemical conditions of preetching treatment for alloys containing the  $\beta$ -phase cannot eliminate hydrogenation completely, they can reduce it substantially. Hydrogenation of  $\alpha$ -alloys and those similar to them (OT4-1, OT4, VT4, OT2, and others) during etching is minor [88]. The presence of oxidizing agents — usually nitric acid — in the etching solution contributes to this. Other compounds, such as  $\text{NaNO}_2$  and organic acids, have also been proposed as oxidants.

Unlike semifinished products, which are often pressworked, the scrap is sent for vacuum remelting and the hydrogen is completely or substantially eliminated from it. Hydrogenation resulting from etching is therefore less important for scrap than it is for semifinished products.

A number of published reports deal with the successful use of electrolytic etching in an aqueous solution containing HF,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and an iron or aluminum sulfate additive for treatment of oxidized semifinished products [89]. An advantage of this method is the possibility of removing the scale without etching away metal. Electrolytic etching is not suitable for processing scrap, since it requires the use of comparatively expensive equipment and the bath must be loaded with material having a certain configuration.

A combination of etching and ultrasonic processing has recently been reported highly effective for stainless steel [90,

91]. The etching time is sharply reduced. The ultrasonic transmitters are attached either to the body of the etching tank or to a water-filled case in which this tank is immersed. Ultrasonic etching obviously merits study for titanium, since titanium is a considerably more expensive metal than stainless steel and the design complication of the etching baths for titanium may be economically justifiable.

#### Melting of Scrap

After preparation for melting, the scrap is introduced into the furnace in several ways: it is pressed, sintered, or melted together with titanium sponge to produce a consumable electrode or introduced directly into the melting space of the furnace.

It has been established in practice that up to 30-35% of chips or small scrap can be added to a charge of titanium sponge for pressing of consumable electrodes. As we noted above, trimmings cut with toothed blades can be introduced into the charge in amounts up to 50%. Pressing of consumable electrodes containing scrap requires the use of hydraulic presses with large loading chambers that are capable of generating rather high specific pressures in the vertical and horizontal directions. For example, the pressure in the vertical direction reached 3000 tons and the horizontal pressure 1200 tons when consumable electrodes were pressed with up to 30% of scrap into  $150 \times 150 \times 500$ -mm blocks; the bulk weight of the blocks was  $3.5-3.8 \text{ g/cm}^3$ . The blocks were welded with titanium wire in an argon atmosphere to produce consumable electrodes of the necessary length [6].

Small scrap to be introduced into consumable electrodes can be pressed separately. In this case, the chips require preliminary annealing, an operation that requires much time and work. A specific pressure of  $2.3 \text{ tons/cm}^2$  is required to press chips into briquettes 100 mm in diameter; this is 2.5 times the specific pressure needed to press sponge [92]. It has been suggested that unannealed chips be pressed after adding 25-50% of sponge to them. (5)

Footnote (5) is on page 598.

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Subsequently, a technology was developed for pressing titanium chips into briquettes weighing up to 1.5 kg without introduction of titanium sponge into the charge; this lowered the cost of briquetting and, accordingly, that of smelting out an ingot [93].

The pressed briquettes are arranged around a central core produced by casting or sintering. The briquettes are welded or strapped to the core.<sup>(6)</sup> Briquettes made with appropriate holes in the center can also be dropped on over the core.<sup>(7)</sup>

There are a number of proposals for consumable-electrode designs that make it possible to introduce sheet and lump scrap into the electrodes. For example, it has been proposed that sheet scrap be cut up into squares or rectangles, pressed, and welded together with longitudinal vertical strips and angle pieces.<sup>(8)</sup> Sheets can also be cut into long strips which are used to weld up an electrode base whose length equals that of the electrode. Long overlapping pieces of scrap are laid on this base, bound with titanium-strip hoops, and secured by spot welding.<sup>(9)</sup> It has also been suggested that the core of the consumable electrodes be made from briquetted small scrap, which is loaded into boxes with the proper cross-sectional dimensions. Long pieces of scrap strip are wrapped around this box and bound together with titanium hoops.<sup>(10)</sup>

A number of consumable-electrode designs provide for the use of a sheet-titanium shell with a bottom plate. To keep the scrap loaded into the box from exerting too much pressure on the bottom plate, several sheet-metal shelves are placed at various heights inside the shell. The scrap placed in the shell may be of arbitrary shape.

Another proposal calls for a core made from strips or rods. The core is placed inside a titanium-shell shell, and the free space between them is filled with small scrap — chips, filings, trimmings, etc.<sup>(11)</sup>

Consumable electrodes containing up to 25-30% of chips can also be made on broaching presses by loading the charge into the press container in small portions. When more than 30% of chips

Footnotes (6), (7), (8), (9), (10) and (11) are on page 598.

are introduced into the electrode, there is a danger that it will break in the furnace during melting as a result of loss of mechanical strength.

The following method of utilizing scrap is proposed in a number of patents.<sup>(12)</sup> The scrap is treated with hydrogen for several hours under a pressure of about 0.5 atm at 550-800°C to cause the metal to absorb 1-2% (by mass) of H<sub>2</sub>. The holding time depends on the amount of metal in the charge and the masses of the fragments. The hydrogenated material is ground up in conventional crushers until fragment size does not exceed 12 mm.

The crushed material is mixed with sponge in amounts such that the content of secondary metal in the charge will not exceed 50%, and blocks are pressformed and welded together to produce consumable electrodes. The latter contain less than 1% H<sub>2</sub> when this charging procedure is followed. If such an electrode is melted in an arc furnace at a residual pressure below 1 mm Hg, the hydrogen content in the first-remelting ingot will not exceed 0.01%, which is less than the acceptable content. The evolved hydrogen takes along with it impurities that usually concentrate at the wall of the crystallizer and spoil the ingot's surface. It is therefore advisable to pump the arc furnace with vacuum pumps whose operation is not impaired by solid particles in the exhausted gas.

It follows from the above that certain difficulties are encountered in the fabrication of consumable electrodes that contain scrap. Measures that make it possible to avoid these difficulties have therefore gained a certain currency in practice.

One such measure is to sinter the consumable electrode in a steel pipe loaded with scrap fragments of various sizes, the spaces between which are filled with sponge.<sup>(13)</sup> Then the loaded pipe is held in a vacuum or an inert-gas atmosphere at 930-1060°C or in an ordinary atmosphere after first welding it shut at both ends. Up to 90% of the mass of the electrode may be composed of scrap if an appropriate variety of fragment sizes is selected (the rest is sponge).

Footnotes (12) and (13) are on page 598.

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The steel case is removed from the electrode after it has been sintered.

Disadvantages of this electrode-making process are the long sintering time, contamination of the electrode by iron, and the need to install special furnaces.

Electrodes can also be sintered in ordinary arc furnaces with nonconsumable graphite electrodes (see Chapter 20). In this case, the scrap is loaded into a separate hopper, from which a feeder conveys it to the graphite electrode in a certain ratio with sponge [2, 21].

If necessary, the consumable electrode may consist exclusively of lump scrap. After treatment to remove scale, the fragments are welded together in an inert atmosphere after stacking them in such a way that the electrode obtained from them will have a more or less regular geometric shape (Fig. 122). The weld seams joining the pieces of scrap must be relatively large in cross section, since the electric current does not flow through the entire cross section of such an electrode, but preferentially through the weld seams [94].

It has also been proposed that the consumable electrode be made from lump scrap fused in an arc furnace with a horizontal crystallizer. The first step is to load the crystallizer with the lump scrap. The crystallizer is then moved under a consumable electrode to melt the scrap fragments.<sup>(14)</sup> Shortcomings of this method include the complexity of the process and the impossibility of making large consumable electrodes.

Since most titanium is produced in the form of twice-remelted ingots, it is most rational to introduce the scrap into the first-remelting ingot. For this purpose, the furnace is fitted with a scrap hopper from which certain amounts of scrap are fed into the molten-metal pool at periodic intervals. It has been established in practice that when the charge of lump scrap represents about 30% of the pool volume, a higher gas content in the scrap produces very little scatter of the ingot's ultimate-strength values along its height; the variations are no greater than those due to the

Footnote (14) is on page 598.

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Figure 122. Consumable electrode welded up from lump scrap.

able electrode is secured to the crank of the furnace's rotating electrode holder has been developed to eliminate this deficiency. The scrap is fed in at the times when the clearance between the electrode and the crystallizer wall under the loading chute has been increased to its maximum by rotation of the electrode holder. As a result, the scrap is discharged into the melting space with the arc burning. To simplify the design of the current supply, the electrode holder is rocked through an angle of almost 360°, so that current can be brought to it by means of flexible bus-bars. (15)

Footnote (15) is on pages 598 and 599.

composition nonuniformity of the sponge.

An arc furnace adapted for introduction of scrap into the pool is described in [2]. This furnace is equipped with two batchers from which the charge is fed to opposite sides of the electrode to improve the composition homogeneity of the ingot. The batcher is an airtight drum with sixteen sections, fifteen of which can be loaded with fragments of charge of varying composition and dimensions. The sections are unloaded one after another through a hole in the bottom disk of the drum, dropping into a chute that sprinkles the charge into the crystallizer.

However, this method of introducing lump scrap into the metal pool involves certain inconveniences: before loading the scrap into the furnace, it is necessary to quench the arc and raise the consumable electrode, and this lowers furnace productivity. A new furnace design in which the consum-

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Since it is necessary to deliver the scrap lumps into the furnace via a feeder, these lumps must have definite shapes and sizes, and this requires not only preliminary cutting, but also forging down. Thus, the operation of introducing the scrap into the consumable electrode is eliminated at the cost of additional processing of the scrap. And titanium oxidizer most rapidly under acetylene cutting and forging work.

The above indicates that remelting of titanium scrap in arc furnaces with a crystallizer involves certain difficulties and inconveniences. For this reason, despite the substantial progress that has been made in improving these furnaces, work continues on other furnace designs — crucible and melt-lined furnaces.

Use of these furnaces might substantially increase the size of the molten-metal pool in the furnace, and this would make it possible to load it with scrap of any form in substantial masses, i.e., it would be unnecessary to cut and forge the scrap.

Only induction- or arc-heated furnaces will be of practical interest in view of the high melting point of titanium.

The basic difficulty encountered in designing an induction furnace for smelting titanium consists in selection of the crucible material. Study of the interaction of various carbon-containing materials with molten titanium has shown [68, page 375] that even the use of compact graphite with sealed pores does not eliminate carbonization of the molten metal.

To eliminate carbonization of molten titanium in a graphite-crucible induction furnace, it has been proposed that a magnetic field be set up in the furnace to force the liquid metal to contract away from the crucible walls. A tablet of titanium was first melted onto the bottom of the crucible. About 2.5 kg of the metal were melted in a 65-kW furnace. The carbon content in the ingots rose from 0.025 to 0.060% as a result of melting in the more successful experiments and to 0.11-0.15% in the less successful ones. Carbonization was more significant in ingots weighing 12 kg [95]. It was later reported that this method had

been tested successfully in smelting of titanium-alloy scrap, and had produced metal suitable for many engineering purposes, including the making of forgings [96]. As for carbon-free materials, early reports to the effect that  $\text{ThO}_2$  and  $\text{ThO}_{1.5}$  and even  $\text{ZrO}_2$  were stable against attack by molten titanium have not been confirmed [68, page 375; 97, 98].

It has been reported<sup>(16)</sup> that titanium scrap can be refined in induction furnaces with crucibles made from pastes of the following compositions, in %: 80  $\text{ThO}_2$ , 10  $\text{Y}_2\text{O}_3$ , 10  $\text{ZrO}_2$ , 85  $\text{ThO}_2$ , 10  $\text{HfO}_2$ , 5  $\text{Y}_2\text{O}_3$ , graphite impregnated with a melt consisting of 90% Th + 10% Hf and then baked out at temperatures no lower than 1650°C. The reliability of these reports is doubtful.

Work is being done on the design of an induction furnace with a water-cooled copper crucible [99, 100]. To reduce power losses, the crucible is divided into segments that are electrically insulated from one another. It has been proposed that this furnace be used for continuous smelting of titanium scrap and pouring of the molten metal into chill molds. Strong electromagnetic agitation of the molten metal is supposed to ensure homogeneity of composition in the resulting ingots. It is advisable to use a plasma torch to apply a layer of nonconductive refractory material, e.g., an oxide, to the inner surface of the sectioned crucible. This will reduce the danger of current flowing through the metal from one segment to another and will reduce heat losses considerably.

Much attention has recently been devoted to the development of arc-furnace designs for melt-liner smelting. Furnaces of this type have large molten-metal pools, and this makes it possible to use them as smelting machines in the production of fancy titanium castings; the large pool makes it possible to load lump or briquetted scrap without going through the stage of converting it to consumable electrodes. As we have seen, certain difficulties are still encountered in the preparation of consumable electrodes in spite of the numerous proposals.

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The crucible of the melt-lined furnaces is usually made of copper and lined with a refractory or graphite. As a result of strong cooling of the crucible, a layer of solid metal — a "floor" — forms on the surface of the lining and prevents the molten metal from coming into contact and reacting with it. To improve operating safety, the crucible is cooled with helium or water run through an external coil.

With proper adjustment of crucible dimensions to furnace power, molten metal may make up about 80% of the total amount of metal in the furnace. This makes it possible to smelt titanium scrap of all forms in furnaces of this type [26].

Nonconsumable or consumable electrodes may be used in smelting. The consumable electrode is made as large as possible in diameter, since this ensures relatively small heat losses by radiation from the pool and makes the pool itself larger in volume [4, 101]. The arc is not put out during pouring in late models of these furnaces. Melt-lined furnaces have smelting rates of 3-6 kg/min at a current of 14 thousand amperes, and the specific power consumption is 2.3 kW·h/kg [102].

A series of vacuum-arc melt-lined furnaces have been developed for intermittent smelting of titanium and titanium alloys in crucibles holding up to 4 tons of the ready-to-pour metal [48].

Figure 123 diagrams the construction of one melt-lined arc furnace for smelting titanium scrap [103]. The stainless-steel smelting crucible, which is about 900 mm in diameter and 530 mm high, holds 1050 kg of titanium, of which 225-400 kg may be in the molten state. The molten-metal capacity of the crucible is determined by the thickness of the melt liner.

An argon atmosphere is used for smelting. The first loads of material are consumed in building up the melt liner in the crucible. During the course of smelting, the charge containing titanium scrap is fed into the crucible in 22-45-kg portions through a charging device that is also argon-filled. The furnace crucible is helium-cooled for safety.

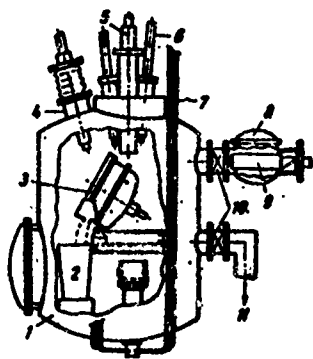


Figure 123. Vacuum-arc furnace for melt-liner smelting of titanium. 1) Furnace shell; 2) mold; 3) crucible; 4) auxiliary electrode; 5) consumable electrode; 6) nonconsumable electrodes; 7) bus to rectifier; 8) charging mechanism; 9) charging ladle; 10) vacuum valves; 11) pipe fitting to vacuum pump.

before the metal is to be poured into the mold; it then serves to heat the head of the ingot and eliminate pipe.

During smelting, the residual pressure in the furnace is lowered to  $10^{-4}$  mm Hg. Ingots weighing up to 180 kg were produced in tests of the furnace. It is claimed that this weight could be doubled.

For production of ingots weighing about 200 kg, the total smelting time, including the time to evacuate the furnace before argon filling, runs to 75-90 minutes. The smelting cycle is slightly longer for larger ingots. Melt-liner smelting produces homogeneous metal, since a large amount of metal is in the molten stage at any given time and is also being vigorously agitated.

It has been reported that the firm Remkru (USA) has built an experimental melt-liner furnace with a capacity of 900 kg for remelting titanium scrap in large pieces [104].

Four nonconsumable tungsten electrodes with thoriated caps are used to melt the charge. After melting, a vacuum is set up in the furnace to degasify the molten metal.

Since tungsten electrodes tend to break in a vacuum, they are switched off during this period, during which melting is continued by using a titanium consumable electrode about 230 mm in diameter, which is mounted centrally in the crucible. The fraction of metal produced by melting of the consumable electrode represents about 10% of the total mass of the melt.

An auxiliary tungsten electrode is used to melt the crust of metal in the crucible's pouring lip just

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The advantages of melt-lined furnaces include: a) composition uniformity of the metal, because of the large size of the molten pool; b) purity of the metal; c) the possibility of remelting scrap in large pieces; d) short smelting times.

Since melt-lined furnaces are used not only to smelt scrap, but also in installations for fancy titanium casting, which are coming to increasing use, much attention will evidently be devoted to improvement of the designs of these furnaces.

It is efficient to deoxidize the metal in the same process in which it is smelted with scrap. We indicated above that pressworking of titanium, which requires heating it to high temperatures, results in the formation of an oxygen-rich surface layer up to 1 mm thick or thicker. At the same time, when as much as 50% of scrap may be returned to the melt, it is necessary to eliminate oxygen from it as thoroughly as possible. An elementary calculation shows that the removal of a one-mm-thick layer even from a comparatively large scrap fragment results in an 8-10% weight loss from this fragment. Moreover, this substantial waste of metal is accompanied by heavy consumption of etchants. Hence the great importance of finding ways to deoxidize titanium during smelting. Attempts to eliminate oxygen by holding titanium at 1500-1600°C and a residual pressure of about  $5 \cdot 10^{-4}$  mm Hg have not produced the desired results [105].

It has been suggested that up to 5% Ca<sup>(17)</sup> be introduced into the consumable electrode to purify the titanium. However, the calcium oxide that forms has a high melting point (about 2500°C) and is not volatile. It has been reported that a metal that has a stronger affinity to oxygen than titanium and forms a volatile oxide is being used for this purpose. At 1500°C, this metal vaporizes and reduces the titanium oxides in the arc zone; the vapor of the new oxide is removed from the furnace by evacuation. The firm Mallory-Sharon uses this process on an industrial scale to smelt out titanium ingots up to 300 mm in diameter [106]. The proposal that one of the rare metals be used as an additive is supported by reports to the effect that titanium and other high-melting metals can be deoxidized by thorium, gadolinium [107].

Footnote (17) is on page 599.

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and even misch metal.<sup>(18)</sup> Misch metal would appear to be most attractive from the economic standpoint, since it is relatively cheap and only 1-2% need be added.

Comparison of the heats of formation of oxides, calculated for 1 g-atom of oxygen [68, page 481], indicates that titanium could be deoxidized by cesium, lanthanum, neodymium, or praseodymium, i.e., by precisely those rare-earth metals that are used to make misch metal. Exploratory tests have indicated that the oxygen content in titanium can be lowered by introducing zirconium, yttrium, or gadolinium into consumable electrodes as deoxidizing additives. The use of boron, which was proposed as a titanium deoxidizer,<sup>(19)</sup> gave unsatisfactory results [108].

#### Ways to Reduce Production of Scrap

Improved utilization of titanium scrap requires improvement of the technology by which it is processed. The number of technological operations must be reduced, ingots and blanks must be heated in neutral atmospheres, and rejection rates must be lowered. This will reduce the amount of scrap that is generated and the extent to which it is oxidized. This problem merits separate attention; we shall limit ourselves here to only a few examples that indicate the scope of the possibilities open in this direction.

The firm ICI (Great Britain) has stopped roughing titanium ingots, with the result that the amount of scrap produced has been cut by 5-6% [58]. Curtiss-Wright presses certain jet-engine parts directly from titanium-alloy ingots, bypassing the forging operation. This gives a substantially lower reject rate, and costs are cut 25-40% [109].

Higher useful-product yields than those cited above have also been reported in the manufacture of titanium products, e.g., 53% (of ingot mass) for aircraft parts made from titanium sheet. Waste is produced in the following forms: initial material 9%, blank trimmings 15%, stamped-sheet trimmings 21%, small scrap 2% [110].

Footnotes (18) and (19) are on page 599.

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Development of technology and equipment for working titanium and its alloys at elevated temperatures in inert atmospheres and in vacuum is highly important from the standpoint of producing substantially less scrap. For example, hydrocarbon vapors have been proposed as protective atmospheres.<sup>(20)</sup> When a specimen of technical titanium (0.025% O<sub>2</sub>) was heated for 30 min at 800°C in butane vapor and then held for 1 hour at 850°C in air, the oxidized-layer thickness was 0.1 mm, as against 0.35 mm for an untreated specimen. The oxidized-layer thicknesses were 0.1 and 1.0 mm, respectively, for specimens of Ti8Mn alloy. The protective effect is explained by the formation of a thin layer of titanium carbide on the surfaces of the specimens. Recipes have also been suggested for protective coatings — e.g., salts that form a vitreous coating on heating to 800°C [111, 112]. According to [113], coating the ingot with an acid aluminosilicate wrapper before heating lowers the hydrogen and oxygen contents in the titanium by a factor of 3-4. The ingots are rolled together with the protective coating, which is then etched off in an alkali bath.

Use of these wrappers not only protects the ingot from oxidation, but also retards its cooling during pressworking. Practical experience indicates that the use of wrappers lowers rejection rates and simplifies the design of the heating furnaces.

By way of controlling titanium-ingot oxidation during heating, it has been proposed<sup>(21)</sup> that they be coated prior to forging with a 0.005-0.025 mm thickness of electrolytic nickel, on which a layer of chromium 0.005-0.010 mm thick is overlaid.

Development of secondary titanium alloys (and fields for applying them), not only in the form of semifinished pressworked products, but also in the form of fancy castings, the manufacturing technology of which is continuously being improved, is highly promising [114].

Footnotes (20) and (21) are on page 599.

| Manu-<br>script<br>Page<br>No. | Footnotes  | Manu-<br>script<br>Page<br>No. |
|--------------------------------|--|--------------------------------|
| 561                            | <sup>1</sup> For brevity, we shall use the term "titanium" in the present section to imply both titanium and titanium-based alloys.                              | 592                            |
| 568                            | <sup>2</sup> Henceforth in this chapter, the term "scrap" will refer to certified scrap.   | 595                            |
| 579                            | <sup>3</sup> Patent (USA) No. 2,891,286, 1959.   | 596                            |
| 580                            | <sup>4</sup> For brevity, we shall henceforth refer to a melt consisting of a mixture of pyrophosphoric and orthophosphoric acids simply as pyrophosphoric acid. | 597                            |
| 586                            | <sup>5</sup> Patent (USA) No. 2,837,773, 1958.   | 597                            |
| 587                            | <sup>6</sup> Patent (British) No. 786,525, 1957.   |                                |
| 587                            | <sup>7</sup> Patent (USA) No. 2,843,921, 1957.   |                                |
| 587                            | <sup>8</sup> Patent (USA) No. 2,792,621, 1957.   |                                |
| 587                            | <sup>9</sup> Patent (USA) No. 2,886,883, 1959.   |                                |
| 587                            | <sup>10</sup> Patent (USA) No. 2,818,672, 1959.  |                                |
| 587                            | <sup>11</sup> Patent (USA) No. 2,867,895, 1959; No. 2,893,113, 1959.   |                                |
| 588                            | <sup>12</sup> Patent (British) No. 900,216, 1962; patent (USA) No. 2,992,094; patent (West German) No. 1,131,894, 1962.  |                                |
| 588                            | <sup>13</sup> Patent (USA) No. 2,753,262, 1956.  |                                |
| 589                            | <sup>14</sup> Glazunov, S.G. et al. Author's certificate (USSR) No. 108,448, 1958.   |                                |
| 590                            | <sup>15</sup> Il'ichev, N.V. et al. Author's certificate (USSR) No.  |                                |

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111,102, 1957; Glazunov, S.G. et al. Author's certifi-  
cate (USSR) No. 122,226, 1959.

<sup>16</sup>

592 Patent (USA) No. 3,079,451, 1963.

595 <sup>17</sup>Patent (USA) No. 2,819,158, 1958.

596 <sup>18</sup>Patent (West German) No. 1,030,036, 1958. Patent (USA)  
No. 2,997,219, 1961.

596 <sup>19</sup>Patent (West German) No. 1,081,237, 1961.

597 <sup>20</sup>Patent (USA) No. 2,865,797, 1958.

597 <sup>21</sup>Patent (USA) No. 2,900,715, 1959.

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Symbol List

| Manu-<br>script<br>Page<br>No. | Russian | When<br>Typed | Meaning   |
|--------------------------------|---------|---------------|-----------|
| 568                            | r       | s             | sponge    |
| 568                            | n       | r             | remelting |
| 568                            | o       | s             | scrap     |

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## Chapter 22

### FUNDAMENTALS OF TITANIUM POWDER METALLURGY

Titanium powder produced by the hydride-calcium and calcio-thermic methods is the most suitable material for powder metallurgy, and is now acquiring steadily increasing importance.

As we know, titanium is used in the compositions of many complex multicomponent alloys for various applications. These alloys are usually produced by vacuum smelting or, much more rarely, by smelting in inert-gas atmospheres. In view of the difficulty of finding crucible materials that might be used in smelting, such complex techniques as floating-charge smelting, arc smelting in a water-cooled copper crystallizer, and even submerged-arc smelting are currently in use.

These smelting methods produce metal with a minimum of contamination, but it is difficult to use them to obtain alloys with uniform composition. For example, in attempts to produce high titanium-copper alloys, the basic mass of the titanium powder floats to the surface of the molten copper [115]. Moreover, a substantial amount of the metal is wasted in roughing the resulting ingots.

Powder metallurgy makes it possible to obtain homogeneous metallic alloys of a given composition from an extremely wide variety of components in a broad range of component proportions. There is practically no wastage of metal during the conversion

from powder to the pressformed blank.

In addition to the hydride-calcium and calciothermic processes used to make titanium powder, we might mention hydrogenation of the compact metal with subsequent crushing and vacuum evaporation of the hydrogen, fused metal spraying, fusion electrolysis, and deposition of the powder from the gaseous phase. The last two methods, and especially the combined-oxide reduction process [116, 117] are also at the same time useful in the production of titanium-based alloys in powder form.

The powders must have certain grain sizes in order to minimize porosity in the products. It may be assumed in first approximation that powder grain sizes should not exceed 0.6 mm for normal working conditions [118].

The London Iron and Steel Institute reports [119] that blanks made from metal produced by the hydride-calcium method are of considerably better quality than blanks made from coarser magnesiothermic metal.

The process of making finished products from titanium and titanium alloys consists of pressing and sintering of the powders.

There are currently three basic methods of pressing: hot pressing in graphite molds, cold pressing with various types of hydraulic and mechanical presses, and hydrostatic pressing at normal temperatures or isostatic pressing for high temperatures.

The conviction that large billets of material could not be produced by powder metallurgy prevailed for a long time [120-123]. This impression had been gained in work with ordinary cold hydraulic presses, where pressing of large billets produced briquettes with vertical and sectional density nonuniformity, so that the molds were distorted even to the point of cracking during sintering.

As long ago as 1955, however, the American firm Brat reported that it had found a hot-pressing technique by which rather large shaped titanium and titanium-alloy workpieces could be made. They weighed up to 50 kg and had diameters up to 228 mm [124]. The hydrostatic-pressing method proposed by Skaupy [125], which can

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be used to produce very large blanks (100-250 kg and more) with uniform density in all sections, has recently been adapted and introduced into the industry on a broad scale. The elaboration of this method that made its industrial use possible in the USSR is due to B.A. Borck et al. [126]. The essentials of the method are as follows: the metal powders are tamped into a waterproof, plastic (e.g., rubber) shell of the desired shape and subjected to three-dimensional hydrostatic compression in special liquid- or gas-filled presses. Figure 124 presents a schematic drawing of one such press. It consists of a thick-walled cylinder 2, which is made from alloy steel, with cover 4 and high-pressure pump 1. The cover has an arrangement for suspending the piece 6 to be pressed and an air valve 5. The cylinder is filled with water or oil. The system pressure generated by pump 1 is monitored at manometer 3.



Figure 124. Diagram of hydrostatic pressing machine.



Figure 125. Extrusion container.

To impart a definite shape to the pressed blanks, a rubber bag filled with the powder is enclosed in a rigid perforated frame or sleeve of the appropriate shape and pressed. Figure 125 shows one device used for pressing cylindrical blanks.

This figure shows the rubber bag 1, which is placed in the perforated metallic sleeve 2. Caps 3 are placed over the ends of the sleeve and secured with elastic bands 4.

In all press types, the pressure applied depends on many conditions. Most important among these are the grain size of the

powder, its component proportions, and the size of the blanks. It may be assumed as a point of departure that a pressure of 500-1000 kgf/cm<sup>2</sup> is sufficient for pressing pure titanium; the pressures for powder mixtures are adapted for each specific case. Normal linear shrinkage for hydrostatic pressing of hydride-calcium titanium is about 40%.

The pressed blanks are sintered at a residual pressure of 10<sup>-3</sup>-10<sup>-4</sup> mm Hg. A hard vacuum is provided with two objectives: the most thorough possible removal of such impurities as hydrogen and magnesium from the titanium and protection of the metal from oxygen and nitrogen. Many sets of conditions for sintering pure titanium and its alloys have been proposed. Kroll [127] used a stepped sintering process: first in a vacuum, and then in argon. Dean states that 16 hours of sintering in a vacuum at 950-1000°C is sufficient for 30-mesh powders [118]. Sintering for 5-6 hours at 1400-1450°C should be regarded as the optimum for pure titanium. The residual porosity in the blank after such sintering does not usually exceed 2-3%.

As a rule, the sintering temperatures for titanium-based alloys must constitute about 80% of the alloy's melting point.

Below we list optimum temperatures for sintering certain titanium-based alloys in °C [128]:

|                                  |                                  |
|----------------------------------|----------------------------------|
| TiH <sub>2</sub> + Cr . . . 1300 | TiH <sub>2</sub> + Co . . . 1100 |
| TiH <sub>2</sub> + Mo . . . 1300 | TiH <sub>2</sub> + Fe . . . 1100 |
| TiH <sub>2</sub> + W . . . 1300  | TiH <sub>2</sub> + Ni . . . 1000 |
| TiH <sub>2</sub> + Mg . . . 1200 |                                  |

If sintering is done at the above optimum temperatures, the disagreement between the measured and theoretical densities of the resulting alloy specimens does not exceed ±0.15%. It is reported in published papers of the London Iron and Steel Institute that the optimum temperature for production of Ti-Cr and Ti-Mo alloys is 1300°C and that the sintering time is 8 hours. These conditions produce blanks with a residual porosity <2.0%.

Many different furnace designs are used to sinter powdered materials.

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Horizontal [129] and vertical [130] vacuum furnaces are in use.

To eliminate the disadvantages associated with the sintering of large blanks in resistance furnaces (the rather steep temperature gradient between the heater and the blank being sintered, which may cause a sinter crust to form in the surface layers and impede desorption of gases), recourse is taken to induction-heated vacuum furnaces (frequency 2500 Hz) [131]. In such furnaces, thermal energy is generated directly in the blank to be sintered, so that there is no temperature gradient resulting from heat transfer from the heater to the blank.

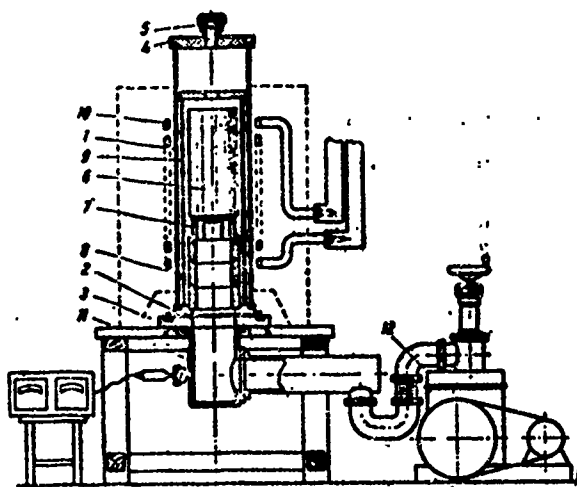


Figure 126. Powder sintering machine.

The sintering installation (Fig. 126) has three main parts: a working chamber and vacuum and electrical systems. The chamber consists of quartz tube 1, which bears through a rubber packing on lower cover 2 with its adapter 3. The top of the pipe is sealed by cover 4, which has an inspection window 5. Vacuum line 11 to pump 12 is connected to the bottom cover. Water-cooled inductor 10, which is made of round-section copper tubing, encloses the quartz tube. Busbars from the high-frequency unit are run to the inductor.

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The blank 6 to be sintered is placed on graphite table 7, which rests on the set of firebrick supports 8. Shield 9 is placed between the blank and the outer tube.

The quartz tube is hoisted out for loading of the blank. Then the supports are installed and the hoist is again used to lower the blank. The top end of the blank is covered with a graphite shield. After insertion of the blank, the shield, outer quartz tube, and cover are mounted. The pump is then switched on, followed by the heating system when the desired vacuum has been reached. After sintering, the reverse sequence of operations is carried out. This furnace can be used successfully for sintering up to a temperature of 2500°C. It may be assumed that forging of the finished pieces is required after sintering in almost all cases.

Recently, much work has been done on the production of titanium sheet, ribbon, and foil by direct rolling of powders [132, 133].

Titanium and its alloys are used in powder metallurgy not only for the production of compact billets, sheets, ribbons, and foils, but also to produce various filtering elements with predetermined porosities and products that contain various passages and internal cavities. In the latter case, appropriate templates made from materials that evaporate during sintering are laid into the titanium powders before pressing. Methods have been devised for hardening of titanium products by introduction of various disperse components, such as  $Ti_5Si_3$ , molybdenum fibers, etc. into the titanium powder<sup>(1)</sup> [134]. In the latter case, the strength of the sintered titanium is increased by a factor of 1.35 over that of the pure metal.

In addition to titanium and its alloys, many titanium compounds ( $TiC$ ,  $TiO_2$ ,  $TiN$ ) are prepared by powder-metallurgical methods, both pure and in compositions with other materials<sup>(1, 2)</sup> [135, 136]. These compounds are used in rocket and aircraft engineering, as well as in radio electronics.

Footnotes (1) and (2) are on page 607.

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| 606 | <sup>1</sup> Patent (French) No. 1,281,754, 1961 |
| 606 | <sup>2</sup> Patent (Japanese) No. 4709, 1959.   |

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ELECTROLYTIC PRODUCTION AND REFINING OF TITANIUM

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## Chapter 23

### BASIC METHODS OF ELECTROLYSIS AND PREPARATION OF THE STARTING MATERIALS

Technical-economic calculations indicate that electrolytic methods can be more economical for production of titanium than the metallothermic methods currently in use. For this reason, research on the electrolytic production of titanium is being expanded steadily.

At the present writing, electrolytic titanium-producing methods are emerging from the stage of scaled-up laboratory experiments. Pilot-plant and even industrial-scale electrolyzer designs are being tested. However, industrial use of electrolytic methods for production of titanium is blocked by major difficulties encountered in the development of electrolysis technology and especially in attempts to find highly productive, economical, and operationally reliable electrolyzer designs.

The broad scope of research on titanium electrolysis and the unremitting search for new electrolyzer designs give reason to hope that the electrolytic process for production and refining of the metal will come to occupy one of the dominant positions in titanium metallurgy.

#### Certain Electrical Properties of Titanium and Its Compounds

Titanium has four valence electrons: two 4s and two 3d. Table 42 gives the inner-orbit structures, ionization potentials,

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and atomic and ionic radii of titanium.

TABLE 42  
Ionization Potentials and Ionic Radii of Titanium

| titanium ion     | structure of outer electron shells | ionization potential, V | ionic radii, Å |
|------------------|------------------------------------|-------------------------|----------------|
| Ti               | 3d <sup>2</sup> 4s <sup>2</sup>    | 6.8                     | 1.46           |
| Ti <sup>2+</sup> | 3d <sup>2</sup>                    | 13.5                    | 0.91           |
| Ti <sup>3+</sup> | 3d <sup>1</sup>                    | 24.6                    | 0.76           |
| Ti <sup>3+</sup> | 3d                                 | —                       | 0.69           |
| Ti <sup>4+</sup> | —                                  | 42.98                   | 0.64           |

\*The ionic radii are given for a coordination number of 6.

Various sources give figures from 47.5 to 54.0  $\mu\Omega\cdot\text{cm}$  for the resistivity of titanium at 0°C. Figure 127 shows the temperature curve of the resistivity of pure (99.9%) titanium. On the basis of resistivity and its temperature dependence, titanium would be classified as a metallic conductor. Many impurities increase the resistivity of titanium, although they do so to a relatively minor degree. For example, [2], the resistivity increase  $\Delta\rho/A$  expressed in  $\mu\Omega\cdot\text{cm}$  (where A is the atomic percentage of the impurity) is 1.8 for niobium, 1.8 for zirconium, and 12 for aluminum.

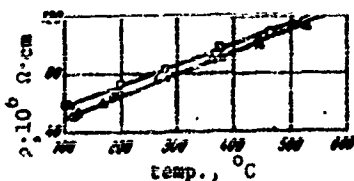


Figure 127. Temperature curves of resistivity  $\rho$  and thermal conductivity  $\lambda$  of pure titanium.

The question as to the type of conductivity and resistivity exhibited by a number of titanium systems and compounds used as materials for soluble anodes is an interesting one.

Numerous studies have shown that most nonmetallic inclusions exist in the monatomic form in transitional metals. On the basis of many properties of the titanium-hydrogen, titanium-nitrogen, and titanium-carbon

systems, a number of investigators [3-7] take the view that

hydrogen, nitrogen, and carbon form interstitial phases in titanium, phases in which the nonmetallic inclusions form metallic bonds, i.e., yield some of their valence electrons to the d-shell of the titanium. Thus, these elements exist as positively charged particles in the crystal lattice. Oxygen does not yield electrons to the d-shell, but, on the contrary, shifts part of the electron cloud toward itself and appears to exist as an anion. Silicon should form covalent bonds preferentially with titanium, and the system may be nonconductive at a certain silicon content in the titanium.

The hydrogen-titanium system has been studied only in the range of low hydrogen contents [8]. It has been shown that up to 1% (atomic) of  $H_2$  causes no marked change in the electrical conductivity of titanium. The titanium-nitrogen system has been studied by various authors [8, 9]. Introduction of nitrogen into titanium has no marked effect on its resistivity. According to G.V. Samsonov [9], titanium nitride has a resistivity of  $86.5 \mu\Omega \cdot \text{cm}$  at  $25^\circ\text{C}$  and a temperature coefficient of resistivity of  $0.375\%/deg$ . The resistivity of titanium carbide is  $59.5 \mu\Omega \cdot \text{cm}$  and its temperature coefficient  $1.52\%/deg$ .

The relationships in the titanium-oxygen system are considerably more complex. At moderate oxygen contents, the  $25^\circ\text{C}$  resistivity of the metal rises by  $12 \mu\Omega \cdot \text{cm}$  for each atomic percent of oxygen [2]. Titanium monoxide has a resistivity of  $0.405 \cdot 10^{-3} \Omega \cdot \text{cm}$  [10]. According to [11],  $Ti_2O_3$  has a resistivity of  $23.3 \Omega \cdot \text{cm}$ , but this figure becomes smaller with rising temperature, reaching  $4.35 \cdot 10^{-2} \Omega \cdot \text{cm}$  at  $700^\circ\text{C}$ . The figures given in [11] are somewhat on the high side. Verwey's data [12] are available for resistivity in the titanium-oxygen system:  $TiO_2$   $10^{10}$ ;  $TiO_{1.995}$   $10.0$ ;  $TiO_{1.995}$   $1.25$ ;  $TiO_{1.75}$   $10^{-2} \Omega \cdot \text{cm}$ .

At the stoichiometric composition, which corresponds to the formula  $TiO_2$ , and at normal temperatures, titanium dioxide does not conduct electricity. An oxygen deficiency creates electronic conductivity, which increases with temperature [13].

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The natural explanation for the resistivity changes in the titanium-oxygen system as functions of component proportions would be that increasing numbers of electrons leave the conduction band to supply oxygen anions as the oxygen saturation of the system increases, thus causing the resistivity of the system to increase.

At moderate silicon contents (up to 10-15%), the titanium-silicon system is a rather good conductor of electricity; at higher silicon contents, system resistivity increases rapidly and it becomes a virtual nonconductor.

Almost no quantitative study has been devoted to the conductivity of titanium chlorides. The proportion of covalent bonds increases and, consequently, conductivity declines in the series  $TiCl_2 = TiCl_3 = TiCl_4$ .  $TiCl_2$  crystallizes in a  $CdI_2$ -type lattice, and  $TiCl_3$  in one of the  $AsI_2$  type. Both salts exhibit ionic conductivity preferentially.  $TiCl_4$  has a tetrahedral structure with zero electrical conductivity. In the 825-900°C temperature range, the conductivity of  $K_2TiF_6$  varies from 2.480 to 3.350  $\Omega^{-1}\cdot cm^{-1}$ .

#### Electrolysis in Aqueous and Organic Media

Equilibrium potentials of titanium in aqueous solutions are given in Table 43.

TABLE 43  
Equilibrium Potentials of Titanium in Aqueous Solutions

| reaction                         | potential, V,<br>acc. to |                  | reaction                                  | potential, V,<br>acc. to |                  |
|----------------------------------|--------------------------|------------------|---|--------------------------|------------------|
|                                  | Omelin<br>[14]           | Lattimer<br>[15] |   | Omelin<br>[14]           | Lattimer<br>[15] |
| $Ti = Ti^{+2} + 2e$              | -1.75                    | -1.63            | $Ti + 2H_2O = TiO_2 + 4H^{+1} + 4e$       | -0.95                    | -0.88            |
| $Ti^{+2} = Ti^{+3} + e$          | -0.37                    | -0.37            | $Ti + H_2O = TiO^{+2} + 2H^{+1} + 2e$     | -                        | -0.88            |
| $Ti^{+2} = Ti^{+4} + 2e$         | -0.16                    | -                | $Ti^{+3} + H_2O = TiO^{+2} + 2H^{+1} + e$ | -0.1                     | -                |
| $Ti + 6F^{-1} = TiF_6^{-2} + 4e$ | -1.24                    | -1.19            |   |                          |                  |

On the basis of these potential values, we might conclude that it is almost totally impossible to produce titanium by electrolysis of aqueous solutions. Nevertheless, a great deal of research is being done on this subject.

The first unsuccessful attempt to electrolyze titanium chlorides was made by Becquerel [16]. Junot [17] also took this approach without success. Knecht [18] showed that titanium chlorides are reduced only as far as the bivalent state. Electrolysis of titanium sulfates in the presence of hydrogen peroxide [19-22] produces lower titanium oxides. Electrolysis of titanium hydroxide in sodium hydroxide solution also yields only thin films of the lower oxides.<sup>(1)</sup> N.G. Kudryavtsev produced only thin films of titanium (3-4  $\mu$ m) at the cathode in alkaline and acidic solutions [24]. Electrolysis of an acidic solution of titanium trichloride with a mercury cathode gives similar results [27, 28].

Experiments in the electrolysis of titanium salts dissolved in their own water of crystallization<sup>(2)</sup> and in the presence of surfactants<sup>(3)</sup> gave unsatisfactory results.

The entire body of experiments that have been carried out up to the present time confirms the practical impossibility of producing titanium by electrolysis of aqueous media.

Use of organic media for the production of metals by electrolysis attracted the attention of researchers long ago [29]. It was assumed that pure metallic deposits could be obtained in oxygen-free or reducing atmospheres. It is acknowledged that the selection of organic media is severely limited from the standpoint of their electrical conductivities.

Research has been done using organic solvents that are liquid at normal temperatures and with fused organic substances. Processes with insoluble and soluble anodes have been studied.

In the former case, representatives of almost all organic-compound classes were tested as electrolytes (usually for electrolysis of titanium chlorides): hydrocarbons, halogenated hydrocarbons, alcohols, ethers, ketones, acids, amines, amides, salts of organic acids, and others [30]. However, all attempts to

Footnotes (1), (2) and (3) are on page 636.

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electrolyze titanium in these atmospheres failed because of the very low solubility or total insolubility of titanium chlorides in them, or because the organic media themselves underwent preferential electrolysis, or because the system was not electrically conductive. In a number of cases, the organic substances oxidized and polymerized on the anode, and this resulted in the formation of electrically nonconductive gums.

Several studies have been devoted to the electrolysis of titanium borohydrides [30], again without success.

Interesting experiments on the electrolysis of titanium compounds in aqueous solutions of sulfanilic acid [25] and titanium tartrate [22, 26] resulted in the formation of cathodic films less than a micron thick. Somewhat better results were obtained from electrolysis of water-and-formalin solutions of  $TiO_2$ .<sup>(4)</sup>

Recently prepared organotitanium compounds dissolve poorly in ordinary solvents; almost all of them are covalent and can hardly be used for electrolysis.

On the whole, it can be stated that electrolysis of liquid organic compounds involves major difficulties and has not yet given hopeful results.

Other media tested for electrolysis have included a number of fused organic-acid salts and fused amines that exhibit rather good electrical conductivity. The compounds electrolyzed were  $TiCl_4$  or soluble anodes containing titanium compounds. The results were not encouraging. It was shown in [32] that, even though  $TiCl_4$  does react with esters of monofunctional acids to form compounds of the type  $TiCl_4-E$  that dissociate in melts, only  $TiCl_3$  is obtained at the cathode when such melts are electrolyzed.

Electrolysis of fused organic media requires further research, because organic melts have a number of advantages over inorganic ones, primarily in their lower melting points.

#### Electrolysis in Fused Inorganic Media

At the present time, titanium is produced most successfully by electrolysis of fused inorganic media. The electrolysis can

Footnote (4) is on page 636.

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be carried out using insoluble or soluble anodes. Melts containing titanium oxides, chlorides, and fluorides have been investigated on a broad scale in insoluble-anode work. Various compounds and alloys of titanium are used as soluble anodes.

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Theoretical analysis and experimental data [33-36]<sup>(5)</sup> indicate that electrolysis in fused salts of oxygen-containing acids, in fused alkalis, oxides, and many other melts cannot produce pure titanium. The selection of fused media is limited chiefly to metal halides. However, not even all of these are suitable for electrolysis. Thus, metals of the 4th and later groups of the periodic system are, as a rule, much more electropositive than titanium; many of their halides are thermally unstable or exhibit low electrical conductivity [37, 38]. The combination of properties found in the chlorides and fluorides of alkali- and alkaline-earth metals renders them most suitable for the present purpose.

NaCl [39, 40],<sup>(6)</sup> KCl, or various mixtures, usually of eutectic composition, are usually used in electrolysis of titanium chlorides: NaCl-KCl, NaCl-LiCl, KCl-LiCl, NaCl-MgCl<sub>2</sub>, NaCl-K<sub>2</sub>TiF<sub>6</sub>, NaCl-KCl-AlCl<sub>3</sub>, NaCl-KCl-CaCl<sub>2</sub>, NaCl-KCl-MgCl<sub>2</sub>, KCl-MgCl<sub>2</sub>-CaF<sub>2</sub>, NaCl-KCl-BaCl<sub>2</sub> [33, 39, 41-45].<sup>(7)</sup> The multicomponent systems are used to lower the electrolysis temperature or increase the solubility of the titanium chlorides in the melt, but they are seldom justified.

Electrolytes used in the electrolysis of K<sub>2</sub>TiF<sub>6</sub> are NaCl, KCl-LiCl, NaCl-KCl [34, 35, 46, 47]; those used in electrolyzing titanium oxides include NaCl, CaCl<sub>2</sub>, and NaCl-CaCl<sub>2</sub>, NaCl-K<sub>2</sub>TiF<sub>6</sub> [48-51], NaCl-CaCl<sub>2</sub>-BaCl<sub>2</sub> [52] and CaCl<sub>2</sub>-CaO;<sup>(8)</sup> soluble-anode work is done with NaCl, NaCl-KCl, NaCl-SrCl<sub>2</sub> [53-58],<sup>(9)</sup> potassium and lithium chlorides, potassium, sodium, and magnesium chlorides, sodium and barium chlorides, and NaCl-K<sub>2</sub>TiF<sub>6</sub> [59].<sup>(10)</sup>

The assortment of salts used as electrolyte components in titanium electrolysis is determined by a number of their properties. An important one is the ability of the salts to dissolve the corresponding titanium compounds. The solubility of titanium

Footnotes (5), (6), (7), (8), (9) and (10) are on page 636.

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compounds in melts has not yet been adequately studied. Certain data on the solubility of titanium compounds in fused salts at 800°C are given in Table 44 [60-69].<sup>(11)</sup>

TABLE 44  
Solubilities of Titanium Compounds in Certain Salts at 800°C, %

| compound                        | solvent |      |      |     |                  |                   |          |          |                        |                                      |
|---------------------------------|---------|------|------|-----|------------------|-------------------|----------|----------|------------------------|--------------------------------------|
|                                 | NaCl    | KCl  | NaF  | KF  | MgF <sub>2</sub> | CaCl <sub>2</sub> | NaCl+KCl | KCl+LiCl | NaCl+BaCl <sub>2</sub> | NaCl+K <sub>2</sub> TiF <sub>6</sub> |
| TiCl <sub>4</sub>               | 0.07    | 0.20 | 0.07 | 0.2 | —                | —                 | —        | —        | —                      | —                                    |
| TiO <sub>2</sub>                | —       | —    | —    | —   | —                | —                 | —        | —        | —                      | —                                    |
| K <sub>2</sub> TiF <sub>6</sub> | —       | —    | —    | —   | —                | —                 | —        | —        | —                      | —                                    |

TABLE 45  
Electrical Conductivities of Salts Encountered in Electrolytic Titanium Production

| salt              | temp. °C | elec- trical conduct- ivity, Ω <sup>-1</sup> ·cm <sup>-1</sup> | salt                            | temp. °C | elec- trical conduct- ivity, Ω <sup>-1</sup> ·cm <sup>-1</sup> |
|-------------------|----------|--|---------------------------------|----------|--|
| LiCl              | 833      | 2.27   | MgCl <sub>2</sub>               | 733      | 1.05   |
|                   | 851      | 6.14   |                                 | 750      | 1.05   |
|                   | 748      | 6.46   |                                 | 774      | 1.13   |
|                   | 801      | 6.23   |                                 | 1013     | 1.13   |
| NaCl              | 850      | 2.22   | SrCl <sub>2</sub>               | 985      | 1.22   |
|                   | 908      | 3.77   |                                 | 1000     | 2.29   |
|                   | 958      | 2.22   |                                 | 1020     | 2.22   |
| KCl               | 800      | 2.19   | NaF                             | 1100     | 2.50   |
|                   | 833      | 2.19   |                                 | 985      | 2.01   |
|                   | 900      | 2.46   |                                 | 1000     | 2.15   |
|                   | 930      | 2.46   |                                 | 1010     | 2.24   |
| CaCl <sub>2</sub> | 795      | 1.66   | K <sub>2</sub> TiF <sub>6</sub> | 1020     | 2.32   |
|                   | 851      | 2.21   |                                 | 825      | 2.48   |
|                   | 928      | 2.24   |                                 | 950      | 2.35   |

Footnote (11) is on page 636.

Table 45 lists the conductivities of certain salts used in the electrolytic production of titanium [38].

The familiar Poincare equation

$$\chi = \frac{pX_1 + qX_2}{p+q}, \quad (1)$$

can be used to determine the electrical conductivities of two-component mixtures in cases approaching ideal solubility; here p and q are the percentages (by mass) of the salts, which have conductivities of  $X_1$  and  $X_2$ , respectively.

At system-component proportions corresponding to the formation of solid phases in the form of chemical compounds, the electrical conductivity of the melt will be quite far below the values computed by this equation.

The most thoroughly studied systems including titanium compounds are chloride systems. However, much remains unclear even concerning these systems. Little study has been devoted to salt systems containing lower titanium chlorides in the presence of  $TiCl_4$  in the gaseous atmosphere. The presence of Ti in four oxidation stages ( $TiCl$ ,  $TiCl_2$ ,  $TiCl_3$ ,  $TiCl_4$ ) is responsible for a series of primary redox reactions, some of which have been evaluated thermodynamically [69]. It has been established that when  $TiCl_4$  reacts with titanium dichloride and titanium, the relative

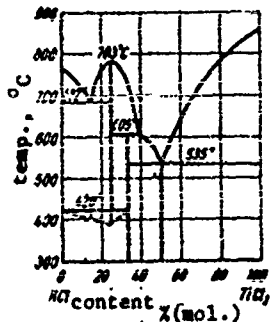


Figure 128. Phase diagram of  $KCl-TiCl_3$  system.

amount of titanium chloride in the melt increases substantially [69, 72, 73]. Studies have been published on the following systems: sodium chloride-titanium trichloride, potassium chloride-titanium trichloride, sodium chloride-potassium chloride-titanium trichloride, potassium chloride-titanium dichloride, sodium chloride-titanium dichloride, magnesium chloride-titanium dichloride, and lithium chloride-potassium chloride-titanium trichloride, and systems consisting of chlorides of sodium, potassium and bi- and

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quadrivalent titanium, titanium metal and sodium, strontium, and other chlorides [42, 61-67, 72].

(1) Complete fusibility curves for the first two systems were given in Fig. 55 (see page 333). They have been confirmed by x-ray structural, microscopic, and analytical study. The fusibility curve of the NaCl-TiCl<sub>3</sub> system has a peritectic at 26% (molecular) of TiCl<sub>3</sub> and 553°C and a eutectic at 40% (molecular) of TiCl<sub>3</sub> and 462°C. The existence of the incongruently melting compound Na<sub>3</sub>TiCl<sub>6</sub> may be regarded as proven.

As we see from Fig. 128, the KCl-TiCl<sub>3</sub> system presents the compound K<sub>3</sub>TiCl<sub>6</sub> melting at 783°C, a eutectic at 15% (mol.) TiCl<sub>3</sub> melting at 682°C, a peritectic at 40% (mol.) TiCl<sub>3</sub> melting at 605°C, and a second eutectic at 50% (mol.) TiCl<sub>3</sub> melting at 535°C.

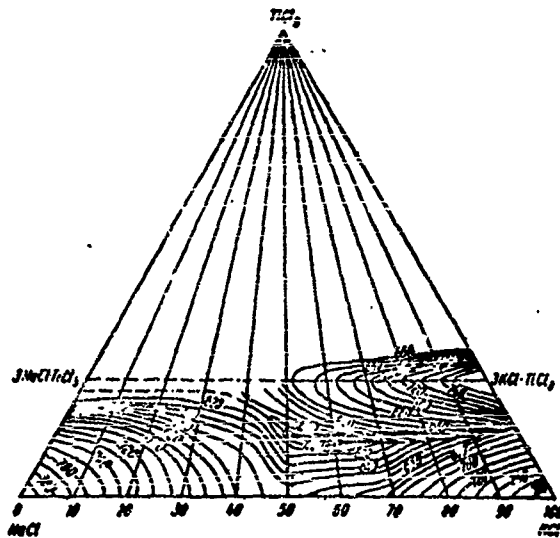


Figure 129. Phase diagram of KCl-NaCl-TiCl<sub>3</sub> system.

M.V. Kamenetskiy [66] also investigated these two systems, obtaining data in close agreement with the above. M.V. Kamenetskiy also studied the KCl-NaCl-TiCl<sub>3</sub> system (Fig. 129) A melt consisting of the chlorides of sodium (40%), potassium (48%), and

titanium [12% (mol.)] has the lowest melting point in this system: 590°C.

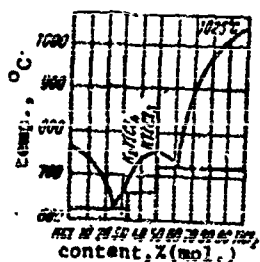


Figure 130. Phase diagram of KCl-TiCl<sub>2</sub> system.

Figures 38, 56, and 130 present phase diagrams for the NaCl-TiCl<sub>2</sub>, MgCl<sub>2</sub>-TiCl<sub>2</sub>, and KCl-TiCl<sub>2</sub> systems.

The existence of titanium-sodium and titanium-potassium chloride complexes in the respective systems and the absence of titanium complexes in the magnesium chloride-titanium chloride system may be regarded as proven.

Interest attaches to certain data on the sodium chloride-potassium chloride-titanium dichloride-titanium trichloride-titanium systems and the sodium chloride-strontium chloride-titanium dichloride-titanium trichloride-titanium systems, which closely resemble those with which researchers deal in most cases [63, 64, 67, 72]. The systems were prepared by different methods. The former was obtained by passing a mixture of argon and titanium tetrachloride into a melt containing metallic titanium, and the latter by electrolytic reduction of titanium tetrachloride in a catholyte consisting of sodium and strontium chlorides (using an alundum diaphragm).

The system formed by sodium, potassium, and titanium chlorides and metallic titanium has been studied for the most part at 700°C. Holding times ranging from 1 to 625 hours were used to bring the system to equilibrium. It was shown that the equilibrium content of titanium dichloride at a molar ratio NaCl/KCl = 1.0 is 87-91% of the total chloride content, which was varied between 1.83 and 8.54% (by mass). Approximately equivalent results were obtained in another study [72].

The second system was investigated in the 650-850°C temperature range with titanium chloride concentrations from 1 to 5%. It was shown that the amount of titanium dichloride in an equimolar mixture of sodium and strontium chlorides represents 81-

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84% (by mass) of the total titanium chloride content.

The systems are three-phased, consist of four components, and therefore have three degrees of freedom; accordingly, their equilibria must depend on component proportions at constant temperature and pressure. It has in fact been found that as the molar ratio  $\text{NaCl}_2/\text{SrCl}_2$  is varied from 4.0 to 0.25, the titanium dichloride content varies from 78 to 93% (by mass). Despite the comparatively low total titanium content in the systems, they are not ideal.

The equilibrium constant of the reaction



diminishes slightly with increasing total titanium content. In [67], K was found equal to  $2 \cdot 10^{-2}$  in fused sodium chloride at  $850^\circ\text{C}$ .

The exothermic nature of this reaction has been confirmed experimentally [64].

The system consisting of 60% lithium chloride and 40% potassium chloride has been investigated in considerable detail with 5 to 12% of titanium trichloride dissolved in it [42]. The cooling curves of this system have a plateau at  $343^\circ\text{C}$  for all concentrations.

The system decomposes above  $460^\circ\text{C}$ , forming two immiscible layers, one of which has a higher trichloride content than the other.

One general remark is in order concerning the chloride systems, which are far from being the only ones to which it applies. At the critical ratio between the titanium and chlorine ionic radii, bi- and quadrivalent titanium ions may form complexes with coordination numbers of 4 and 6, respectively [74]. This explains a number of factors attesting to the existence of complexes of the  $[\text{TiCl}_4]^{-2}$  and  $[\text{TiCl}_6]^{-3}$  types in the melts. On the one hand, formation of such complexes helps increase the solubility of

titanium in the melts, which is beneficial for electrolysis; on the other hand, these complexes increase the resistivity and viscosity of the melts and result in poorer conditions for the formation of large, high-quality titanium deposits on the cathode.

It must be remembered in selecting systems for electrolysis that the stability of these complexes depends, other conditions the same, on the electrostatic properties inherent to the ions of the metals whose chlorides are used as solvents for the titanium chlorides. The higher the ratio between the charge and radius of this cation, the greater is its ability to defeat the titanium in its effort to attract chlorine ions and form structural units with a definite coordination number. For example, sodium and potassium ions have equal charges, but the radius of the sodium ion is smaller and, consequently, it attracts chlorine ions electrostatically with greater force. As a result, it is extremely difficult for the  $[\text{TiCl}_6]^{-3}$  complex to exist in the titanium tetrachloride-sodium chloride system; on the other hand, this complex exists and is quite stable in the potassium chloride-titanium tetrachloride system. The existence of complexes has been established in the sodium chloride-titanium dichloride system, but not in the magnesium chloride-titanium dichloride system.

The above considerations are a basis for rational selection of salt systems for electrolysis.

Complexing is especially important for the quadrivalent titanium ion, which has a very low solubility in fused alkali and alkaline-earth chlorides. L.A. Tsiolkina and M.V. Smirnov [75] found the following solubilities for titanium tetrachloride in fused alkali-metal chlorides at 700°C: 0.014% in lithium chloride, 0.3% in a mixture of sodium and potassium chlorides (1:1), and 1.2% in potassium chloride (by mass). When the fluoride ion, which has a considerably smaller radius than the chlorine ion, is added to the melt, the stability of the titanium complex ions is enhanced. Thus, it was established in this study that addition of fluorides to the melt sharply increases the solubility of titanium tetrachloride. For example, the addition of 15% (by mass) of NaF to an equimolar melt of sodium and potassium chlorides

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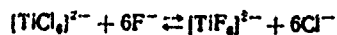
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increases the solubility of titanium tetrachloride to 3.14% (by mass). It was shown that the change in the thermodynamic potential of the reaction in the melt



equals -32.2 kcal/mole.

TABLE 46  
Decomposition Voltage of Salts

| Salt              | Temp. °C | Decomposition voltage V | Salt                            | Temp. °C | Decomposition voltage V |
|-------------------|----------|-------------------------|---------------------------------|----------|-------------------------|
| NaCl              | 877      | 3.38                    | SrCl <sub>2</sub>               | 800      | 3.41                    |
| KCl               | 788      | 3.58                    | K <sub>2</sub> TiF <sub>6</sub> | 650      | 1.8-1.9                 |
| LiCl              | 850      | 3.41                    | TiO                             | 850**    | 2.80                    |
| CaCl <sub>2</sub> | 700      | 3.38                    | TiO <sub>2</sub>                | ?        | 2.06                    |
| MgCl <sub>2</sub> | 700*     | 2.51                    | TiCl <sub>3</sub>               | 800      | 1.80                    |
| TiCl <sub>4</sub> | 820*     | 1.84*                   | TiCl <sub>4</sub>               | 800      | 1.69                    |

\*In fused KCl.

\*\*In fused CaCl<sub>2</sub>.

F.M. Kolomitskiy<sup>(12)</sup> studied the K<sub>2</sub>TiF<sub>6</sub>-NaCl system. It was shown that this system has a eutectic at 64% (by mass) of potassium hexafluorotitanate with a melting point of 530°C.

Titanium dioxide is readily soluble in chloride-fluoride systems, probably as a result of the formation of oxyfluoride complexes.

The decomposition voltages of certain individual salts are given in Table 46 [38].

The decomposition voltages of these salts decrease with rising temperature.

A certain amount of data has been obtained on the equilibrium potentials of titanium and its common alloy components in fused chlorides [65, 76].

M.V. Smirnov and N.A. Loginov measured the equilibrium potentials of titanium against a chlorocarbon electrode in a fused equimolar NaCl-KCl mixture with various titanium-ion

Footnote (12) is on page 636.  
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concentrations: 5.64, 1.40, 0.7, and 0.23% (by mass) at temperatures from 701 to 975°C [126]. The following potential values were obtained:

$$E_{Ti^{+3}}^{\circ} = -2,382 + 4,83 \cdot 10^{-4} T \text{ V}; \quad (3)$$

$$E_{Ti^{+2}}^{\circ} = -2,158 + 3,164 \cdot 10^{-4} T \text{ V}. \quad (4)$$

B.F. Markov and B.P. Podarza [80], who measured the potential of titanium in the same system at 700°C, obtained a value of -1.807 V. The activity-coefficient ratio  $Ti^{+3}/Ti^{+2}$  was found equal to 0.0159.

It was shown in [81] that the potential of titanium in mixed chloride-fluoride melts depends on the fluorine-ion ( $F^{-}$ ) concentration:

$$E = -2,66 - 4 \cdot 10^{-4} T - 3,97 \cdot 10^{-4} T \lg(F^{-}). \quad (5)$$

Experience has shown that when the titanium chloride concentrations in the electrolyte are low, they are practically absent in the chloride sublimates that settle on the cold parts of electrolyzers. The vapor pressures of the chlorides and fluorides of other metals used in electrolysis (Na, K, Ca, Mg) are comparatively small and permit wrong-term electrolysis experiments without any substantial loss of electrolyte.

#### Preparation of Starting Materials for Electrolysis

Normal electrolyzer operation requires that the electrolyte be held at definite concentrations of the materials to be electrolyzed. These materials can be prepared either in the bath or outside of it. Lower titanium chlorides are often used as the titanium-containing compounds for titanium electrolysis.

Methods of preparing lower titanium chlorides outside the electrolyzer were examined above.

There are several methods for preparing the lower chlorides directly in the electrolyzer. The first consists in bubbling a mixture of carbon tetrachloride and hydrogen through the melt or introducing this mixture into a hollow anode immersed in the melt. (13) In this case, it is principally titanium trichloride that is formed in the bath, along with some chlorotitanate. In Footnote (13) is on page 637.

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a second method, titanium tetrachloride is introduced into the cathode space, where it is reduced by the sodium or other metal whose chloride is used in the bath [45, 56, 67]. This method has been improved by introducing an auxiliary cathode into the bath for use in saturating the electrolyte with titanium ions.<sup>(14)</sup>

In the second method, a mixture of titanium trichloride and dichloride is obtained in the electrolyzer. In a third method,  $TiCl_4$  is partially reduced in the electrolyzer on a vanadium heater-catalyst.<sup>(15)</sup>

The first method does not give good results, and for a number of reasons. Most important among these:

a) hydrogen chloride, which attacks the equipment, is formed in the reaction between the hydrogen and the chlorine evolved at the anode;

b) introduction of hydrogen promotes the formation of small cathodic crystals;

c) subsequent separation of the unreacted hydrogen from the inert gases is very difficult.

The third method complicates the design of the bath and is unproductive. Reduction of titanium tetrachloride in the cathodic zone must be regarded as the most successful method in use at the present time.

Leaving aside soluble-anode electrolysis, it may be taken as a general rule that the purity of the cathodic deposit will be equivalent to or slightly lower than the purity of the starting materials.

Direct introduction of titanium fluorides into the bath has not come into practice in the fluoride processes. The material usually used here is  $K_2TiF_6$ , which is injected into the melt before starting the work and can be added during the process up to a certain limit. Although it calls for a series of operations, the preparation of potassium hexafluorotitanate presents no particular technical difficulties. It is usually prepared by reacting highly purified titanium dioxide with hydrofluoric and

Footnotes (14) and (15) are on page 637.

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concentrated sulfuric acids. The resulting titanium fluoride is distilled off into a soda solution, where a hexafluorotitanate precipitate is formed, suction-filtered out of the mother liquor, and passed through two repurifying stages, which consist in dissolving it in hot water (90-100°C), suctioning through a hot filter, and cooling. The water-salt proportions are 8 parts (by mass) of salt to 100 parts (by mass) of water. The crystals thus obtained are dried for 24-30 hours in a vacuum at 85-90°C and stored in hermetically sealed containers [47]. The moisture and titanium dioxide contents in this material are usually around 0.01%.

Titanium dioxide is used for the most part in oxide work. Methods of preparing titanium dioxide will be examined below.

Lower titanium chlorides can be obtained from  $TiCl_4$  by several methods. Titanium, sodium, magnesium, hydrogen, antimony, arsenic, zinc, and lead are used as reducers [41, 55, 108]. For various reasons, the principal reducing agents used are hydrogen, sodium, and titanium.

Titanium tetrachloride is reduced by hydrogen at 1000-1100°C. It is necessary to remove the products from the reaction zone immediately (by chilling) to maintain a steady and adequate shift of the reduction-reaction equilibrium. The following method is effective [41]. A tungsten wire in a quartz sleeve (this heating element may be replaced by an electric arc) is drawn axially through a cylindrical molybdenum-steel flask. The  $TiCl_4 + H_2$  mixture is passed through the flask at 1000-1100°C. The reaction product, titanium trichloride, is collected on the walls of the flask, from which some of it is washed by the stream of unreacted titanium tetrachloride, for subsequent separation by distillation. In this reduction method, about 0.005% of metallic titanium is formed as an impurity in the  $TiCl_3$ .

$TiCl_4$  is usually reduced by sodium to obtain titanium dichloride [55, 108]. The process is run at 650-700°C with a sodium deficiency. The equipment that has been designed for this process takes a wide variety of forms. In one version [108], fused metallic sodium is dripped into a reaction tower. Titanium

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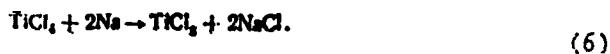
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tetrachloride is also fed continuously into the tower. The rate of reagent inputs is controlled in such a way as to support the reaction



The result of the reaction is a mixture of sodium and titanium chlorides containing about 50% Ti. Sodium chloride is then added to the mixture to dilute it.

Titanium can be used as a reducing agent for the preparation of both titanium trichloride and dichloride. The quantity of either chloride in the reaction mixture depends on temperature and the proportions of the initial components [108, 127, 128]. For electrolysis, it is more convenient to use divalent titanium. The process can be conducted either in reactors that contain only titanium or in reactors that contain molten or solid alkali metal chlorides [52, page 194].

Lower titanium chlorides can be produced with soluble anodes. This process is extremely simple from both the technological and equipment standpoints. It consists in electrolysis of titanium scrap, which is used as a soluble anode at the highest possible cathodic current densities (15-40A/cm<sup>2</sup>). The process temperature range is 750-850°C, and the anodic current densities are 1 A/cm<sup>2</sup> or lower. The titanium chloride concentration in the bath can be lowered to 5-10% in this process; concentration can be increased by combining electrolysis with delivery of dry HCl or TiCl<sub>4</sub> into the bath (Fig. 131).

The next method of producing lower titanium chlorides is based on the reaction



where Me is a metal that is more electropositive than titanium.

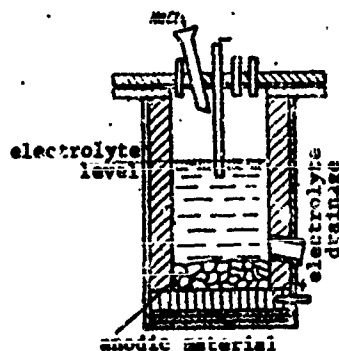


Figure 131. Apparatus for production of lower titanium chlorides.

Ferrous chloride is usually used. The process consists in introducing the ferrous chloride and titanium powder into fused alkali chlorides. The process is usually conducted under an argon atmosphere and with agitation. The time required for completion of the reaction is 1.5-2 hours, after which the electrolyte containing the lower titanium chlorides is separated from a residue consisting of titanium with iron cemented to it [130].

Treatment of titanium with dry gaseous hydrogen chloride at temperatures from 900 to 950°C produces a mixture of lower titanium chlorides and small amounts of titanium tetrachloride, which is distilled off in the course of the process.

#### Methods of Electrolyte Composition Analysis

Methods of analyzing the electrolyte to determine total titanium and its contents of titanium ions of various valences are of great interest for the theory and practice of electrolysis. Finding such methods took a great deal of time, and the work has not yet been completed, but there are now a number of developed methods for analyzing the electrolyte to determine bi-, tri-, and quadrivalent titanium when they are present in it together.

Several methods have been described for the case in which the electrolyte may be assumed to contain no dissolved alkali metals or their subchlorides. Two of these are almost identical [131, 132] and involve separating a small weighed sample of electrolyte into two parts, one of which is dissolved directly in a solution of iron-ammonium alums, while the other is introduced into the alums after first dissolving it in sulfuric or hydrochloric acid. The two solutions are titrated with permanganate. In the former case, trivalent iron is reduced by either bi- or trivalent titanium; in the latter, it is reduced only by trivalent titanium, since the preliminary solution in acid has converted all of the divalent titanium to trivalent. Knowing the content of titanium in the weighed sample, the amounts of  $Ti^{2+}$ ,  $Ti^{3+}$ , and  $Ti^{4+}$  can be found by a simple calculation.

However, both of these methods are approximate, since the titanium dichloride may react with the acid in acidic solutions

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when the lower titanium chlorides are titrated with iron-ammonium alums, releasing hydrogen:



with the result that the analysis gives figures on the low side for  $\text{Ti}^{2+}$ .

Other methods of determining  $\text{Ti}^{2+}$  and  $\text{Ti}^{3+}$  are based on utilization of this last reaction. They consist in measuring the amount of hydrogen evolved in this reaction in acidic solutions; when all of the hydrogen has been released, trivalent titanium is determined in the same solutions [44, 132, page 1415]. The original amount of  $\text{Ti}^{3+}$  is found as the difference.

These methods are more accurate than the preceding ones, although the equipment required is more complex. However, none of these methods takes account of the fact that the electrolyte may, in many cases, contain alkali or alkaline-earth metals or their subchlorides, which are capable of evolving hydrogen and reducing bivalent iron. Dean et al. found that the amount of free metals in the electrolyte and the average valence of the titanium can be found by combining these methods [58].

In analyzing electrolyte, it is necessary to work with it in air for a certain time. This may result in oxidation and hydrolysis of lower titanium chlorides and shift the equilibrium between the components of the melt. One recent study proposes that these effects be prevented by an analytical procedure in which the fused electrolyte is drawn into an L-shaped tube with  $\text{K}_2\text{FeCl}_4$  in one of its arms; after the iron has been reduced by the titanium chlorides in the fused state and without exposure to air, the melt is cooled and titrated [134]. Other methods have also been elaborated [23, 85].

## Footnotes

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- 620 <sup>1</sup>Patent (German) No. 605,551, 1934.
- 620 <sup>2</sup>Patent (USA) No. 1,113,546, 1914.
- 620 <sup>3</sup>Patent (USA) No. 1,885,700, 1932.
- 621 <sup>4</sup>Patent (Japanese) No. 15,202, 1960.
- 622 <sup>5</sup>See also patent (German) No. 150,557, 1903.
- 622 <sup>6</sup>See also patent (USA) No. 2,975,111, 1961; No. 3,002,905, 1961; patent (German) No. 615,951, 1935; patent (British) No. 698,151, 1953.
- 622 <sup>7</sup>See also patent (Austrian) No. 154,266, 1961; patent (British) No. 712,742, 1954; patent (USA) No. 2,975,111, 1961; No. 3,002,965, 1961; No. 2,731,404, 1956; patent (British) No. 678,807, 1951; patent (Japanese) No 3859, 1952.
- 622 <sup>8</sup>Patent (USA) No. 3,003,934, 1961.
- 622 <sup>9</sup>Patent (French) No. 74,709, 1961.
- 622 <sup>10</sup>See also patent (USA) No. 2,898,275, 1959; No. 2,817,631, 1957; patent (Japanese) No. 3705, 1957; No. 5405, 1957.
- 623 <sup>11</sup>Kolomitskiy, F.M., Author's abstract of dissertation, Sverdlovsk, 1957.
- 629 <sup>12</sup>Kolomitskiy, F.M., Author's abstract of dissertation, Sverdlovsk, 1957.

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- 630      <sup>13</sup>Patent (British) No. 698,151, 1953; patent (Japanese)  
No. 5702, 1956.
- 631      <sup>14</sup>Patent (British) No. 712,742, 1954; patent (USA) No.  
2,975,111, 1961; patent (USA) No. 3,302,965, 1961.
- 631      <sup>15</sup>Patent (Australian), No. 7633, 1955; No. 7635, 1955;  
No. 7636, 1955.

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## Chapter 24

### ELECTROLYTIC PRODUCTION OF TITANIUM WITH INSOLUBLE ANODES

#### Electrolysis of Titanium Chlorides

The most suitable environment for electrolysis of titanium chlorides is sodium chloride, either alone or mixed with potassium hexafluorotitanate. These electrolytes, and the former in particular, are least capable of dissolving oxygen, resist hydrolysis, and are comparatively cheap. Coarse-grained deposits can be obtained on the cathode when they are used. Their relatively high melting points do not make these electrolytes any less valuable.

The salts used in electrolysis must be quite free of oxygen and elements that are more electropositive than titanium.

The starting material now most commonly used for electrolysis is titanium tetrachloride. Since  $TiCl_4$  is a covalent compound, direct electrolysis is impossible. It can exist in fused chlorides in the form of complexes of the  $[TiCl_5]^{-2}$  type, which are very slightly soluble and thermally unstable [82-84]. Electrolysis of  $TiCl_4$  in fused media produces highly dispersed cathodic deposits that are not strongly bound to the cathode and have a tendency to become contaminated, especially by oxygen, at all stages of the process. In this case, production of high-grade metal in a single electrolysis run is extremely difficult. The

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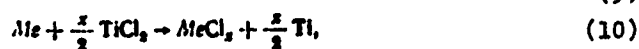
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utilization of titanium tetrachloride in the electrolysis varies from 80 to 100%. The most complete utilization is obtained when the titanium tetrachloride penetrates deep into the layer of electrolyte and at a certain correspondence between the rate of its delivery and the rate of cathodic-metal deposition.<sup>(1)</sup> The process improve when fluorides are present in the melt.<sup>(2)</sup>

Lower titanium chlorides are more suitable for electrolysis. They are easily obtained from  $TiCl_4$ , readily soluble in fused salts, and quite stable at the electrolysis temperatures; they have good electrical conductivity and comparatively low volatility. An undesirable property in the lower chlorides is their high chemical activity. Under the conditions of electrolysis, they react with almost all conventional lining materials [42, 60, 86]. The rate of reaction of the lower chlorides with the lining material probably depends strongly on the presence of oxygen in the bath.

It was generally believed until recently that the cathodic process is preferentially a secondary one [39, 58, 88]:



where Me is sodium, calcium, potassium, strontium, etc., and x is valence.

However, research carried out in recent years has shown that direct electrochemical discharging of titanium ions takes place at the cathode under certain conditions. Most important among these conditions is an adequate concentration of titanium ions of the lower valences in the layer at the cathode. There are data indicating a stepwise nature for the process in which titanium is reduced at the cathode [89].

Chlorine ions are discharged at the anode with formation of molecular chlorine and, in the case of carbon anodes, chlorocarbons as well. CO and CO<sub>2</sub> are evolved simultaneously in the

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Footnotes (1) and (2) are on page 647.

presence of oxides. At a high enough voltage and without diaphragms on the anode, titanium tetrachloride may be released as a result of oxidation of lower titanium chlorides present in the melt by the anodic chlorine.

Titanium chlorides are electrolyzed in inert-gas (argon or helium) atmospheres. The following procedures are usually employed first to free the electrolyte of moisture and occluded gases:

- 1) vacuumizing of the electrolyzer at 400-650°C to a residual pressure of 10-20 mm Hg [42];
- 2) preliminary electrolysis at an auxiliary cathode with a voltage of 1.8-2.0 V across the electrolyzer terminals.

There are also other methods of purifying the electrolyte. One of them is used to remove moisture. It consists in repeated passage of dry hydrogen chloride through the melt. A second method consists in passing carbon tetrachloride through the melt, and is used to clear it of oxygen [41].

TABLE 47  
Optimum Process Indicators in Titanium Electrolysis

| Electrolyte                    | Process temp. °C | Titanium concentration in electrolyte % (by mass) | Cathodic current density A/cm <sup>2</sup> | Current efficiency % | Titanium content in cathodic deposit %, or hardness HB of metal | Literature source |
|--------------------------------|------------------|---|--|----------------------|---|-------------------|
| NaCl                           | 800              | —   | 0.43                                       | 61                   | ~113 HB   | [42]              |
| LiCl + KCl                     | 550              | ~12.0   | 0.8  | 81                   | 99.0  | [43]              |
| NaCl + MgCl <sub>2</sub>       | 750              | ~5.0  | 1.0  | 81                   | 99.5  | [44]              |
| NaCl + MgCl <sub>2</sub>       | 700              | —   | 1.0-1.5                                    | 81                   | 99.5  | [45]              |
| NaCl + SiCl <sub>4</sub>       | 700              | —   | 1.0  | 81                   | 99.5  | [46]              |
| NaCl + SiCl <sub>4</sub>       | 650-730          | ~3.0  | 1.0  | 80-90                | ~110 HB   | [47]              |
| NaCl + KCl + MgCl <sub>2</sub> | 675-700          | ~1.5  | —  | 86                   | 99.3  | [48]              |
| NaCl + KCl + CoCl <sub>2</sub> | 675-700          | ~1.5  | —  | 86                   | 99.3  | [49]              |

<sup>1</sup> Electrochemical current efficiency calculated for quadrivalent titanium.

<sup>2</sup> Patent (Australian) No. 154,266, 1951

<sup>3</sup> Patent (British) No. 678,807, 1951.

<sup>4</sup> Patent (British) No. 734,094, 1955.

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Graphite or tungsten are the usual anode materials, even though they do not fully satisfy all requirements: tungsten gradually corrodes and contaminates the electrolyte, while graphite has an anodic effect at current densities of 0.8-1 A/cm<sup>2</sup> and higher, in which an envelope of gaseous chlorine or chlorocarbons forms on the anode surface and interrupts the passage of current [90]. The anodic effect is usually eliminated by introducing a small amount of oxides into the anodic space.

Many materials have been tested for the cathodes: tungsten, molybdenum, nickel, silver, and a number of others [41-43, 44, 60]. The titanium deposits bond best to a silver cathode. However, this metal is expensive. Steel and nickel cathodes are used. The liquid cathodes - zinc and lead - that have been investigated will hardly be useful in view of the fact that they form hard-to-decompose intermetallic compounds with titanium.

The separating diaphragms used in [45, 91] are highly interesting. The former study used aluminum oxide diaphragms, which, according to the authors, undergo practically no metalization under proper conditions, while graphite diaphragms were employed in the latter case. This case is further interesting for the fact that the electrolysis was conducted with a contact cathode, on which semisintered metal formed at 1305°C. It is acknowledged that this process uses electric power at a high rate (about 77 kW·h per kilogram of titanium).

The influence of the basic electrolysis parameters on the quality of the cathode deposits, the course of the process, and current efficiency has been studied in detail on many occasions. It has been shown that low temperatures, low titanium concentrations in the electrolyte, and high cathodic current densities result in the formation of a fine dendritic powder that clings weakly to the cathode. Not all of the authors describe their processes fully. Table 47 lists optimum data according to the principal published works.

Work with titanium chlorides requires a high voltage across the electrolyzer terminals (usually 9-12 V), which results in high consumption of electric power per unit of production.

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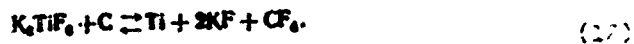
## Electrolysis of Titanium Fluorides

It is known that potassium hexafluorotitanate  $K_2TiF_6$  is the most suitable fluorine compound for electrolysis [92]. It is comparatively easily produced, is a good conductor of electricity and stable in air, and has a low vapor pressure.

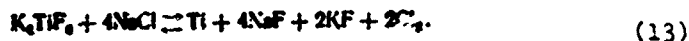
It is not advisable to electrolyze potassium hexafluorotitanate alone. During electrolysis, it is reduced to the compound  $K_2TiF_5$ , after which the electrodes begin to polarize, with the resulting very low current efficiencies. For this reason,  $K_2TiF_6$  is usually dissolved in fused salts for electrolysis.

Electrolysis of potassium hexafluorotitanate in fused media requires that an inert atmosphere be provided. Sodium chloride is the best and most thoroughly understood solvent electrolyte [47]. The bath material is usually graphite, which serves simultaneously as the anode. It is almost impossible to use any of the other materials, since potassium hexafluorotitanate reacts under the conditions of electrolysis with porcelain, refractory clays, glass, and other materials used to line baths. The cathode material is usually steel, which is secured to a nickel or graphite holder above melt level.

According to Drossbach [46, 98], the mechanism of the electrolysis of  $K_2TiF_6$  can be represented in the form of the over-all reaction



Obviously, this equation implies that the process will take place in an electrolyte that is very poor in chlorides. In a chloride-rich electrolyte, the process will evidently take place by the reaction



To eliminate the anodic effect, it is necessary to add small amounts of titanium dioxide in the anode zone. The cathodic process involves discharging of  $Ti^{4+}$  ions formed by the reaction



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The reduction at the cathode is stepwise [93]. It is difficult to make the process continuous, since potassium fluoride gradually accumulates in the bath, raising the melting point of the electrolyte [36, 41]. Regeneration of the fluorine is very troublesome. It requires treatment of the fluorides with concentrated sulfuric acid [94].

The 740-800°C temperature range is the optimum for the electrolysis process. At these temperatures, large laminar hexagonal-packed crystals can be formed on the cathode. At higher temperatures, fine crystals with distorted lattices predominate, and current efficiency declines. Below 700°C, the electrolyte becomes too viscous. The potassium hexafluorotitanate concentration may not be high, although it is highly soluble in sodium chloride [the eutectic point corresponds to a 64% (by mass) content of  $K_2TiF_6$ ]. At high potassium hexafluorotitanate contents in the melt, oxidation reactions occur; they can be represented in general form by the equations



The current efficiency decreases as a result of these reactions. The optimum potassium hexafluorotitanate concentration in the melt is 15-17% (by mass).

The optimum current densities at the cathode are 1-3 A/cm<sup>2</sup>.

Preliminary removal of moisture, occluded gases, and metals that are more electropositive than titanium - iron in particular - from the electrolyte is mandatory in all cases. The minimum bath voltage is 2.6-3 V.

In occasional cases, the titanium produced by this method has exhibited mechanical properties on a par with those of the highest grades of magnesiothermic metal. The chemical composition of the cathodic metal produced in one of the papers cited [47] is characterized as follows: 99.5-99.8% Ti, 0.05-0.1% O<sub>2</sub>, 0.04-0.017% N<sub>2</sub>, 0.03-0.13% C.

In [35], 99.9% pure titanium was produced by electrolysis of  $\text{Na}_2\text{TiF}_6$  in fused sodium and potassium chlorides at 800°C and a cathodic current density of 0.4-1.6 A/cm<sup>2</sup>.

#### Electrolysis of Titanium Oxides

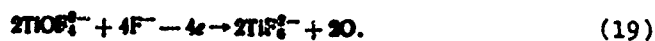
All oxides of titanium and alkali-metal titanates have been tested as starting materials for the production of titanium by electrolysis of its oxygen-containing compounds in fused media. Many fused media have been tested for solution of titanium oxides and their electrolysis, with emphasis on NaOH,  $\text{Na}_4\text{P}_2\text{O}_7 + \text{NaCl}$ ,  $\text{Na}_4\text{P}_2\text{O}_7 + \text{CaCl}_2$ ,  $\text{CaCl}_2$ , cryolite,  $\text{CaO} + \text{CaCl}_2$ ,  $\text{NaF} + \text{KF}$ , alkali-metal phosphates and borates,  $\text{NaCl} + \text{CaCl}_2$ ,  $\text{NaCl} + \text{K}_2\text{TiF}_6$ . The best results were obtained using  $\text{NaCl} + \text{CaCl}_2$ <sup>(3)</sup> and  $\text{NaCl} + \text{K}_2\text{TiF}_6$ , as well as  $\text{CaCl}_2 + \text{CaO}$  [34; 48-50; 52, page 29; 95-104; 106].

Many studies have been devoted to the electrolysis of  $\text{TiO}_2$  in fused  $\text{CaCl} + \text{K}_2\text{TiF}_6$  [48; 49; 52, page 29; 99-104; 106]. The physicochemical properties of the melts have been studied, and some of the authors have attempted to ascertain the mechanism of the process. It was shown in [106] that the electrolysis mechanism differs for different  $\text{TiO}_2$  concentrations in the melt. At high titanium dioxide concentrations, it is reduced at the cathode to  $\text{Ti}_2\text{O}_3$ . Titanium dioxide and sesquioxide then envelop the cathode with a mass resembling the cathodic deposit and not susceptible to further electrolysis. At low  $\text{TiO}_2$  concentrations, titanium is formed in the steady process at the cathode in accordance with the net reaction



with formation of the intermediate complex  $\text{TiF}_6^{2-} + e \rightarrow \text{TiF}_6^{3-}$ , which is a source of titanium ions.

At high titanium dioxide concentrations,  $\text{TiO}^{2+}$  and  $\text{Ti}_2\text{O}_3^+$  ions are discharged at the anode [107]; low concentrations make possible the formation of  $\text{K}_2\text{TiF}_4$ , whose anions are discharged in the reaction



Footnote (3) is on page 647.

The oxygen liberated here reacts with the anode graphite to form  $\text{CO}_2$ .

Less study has been devoted to the electrolysis of titanium dioxide in fused  $\text{CaCl}_2$  [100]. The authors of this paper consider the cathodic process to be secondary in nature:



Effective conduct of this process requires low  $\text{TiO}_2$  contents in the electrolyte, continuous introduction of this oxide into the bath, and periodic changing of the electrolyte as it becomes saturated with  $\text{CaO}$ . Thorough removal of oxygen from the titanium is unlikely in this case. Not even so strong a reducing agent as calcium can reduce the titanium completely.

In addition, oxygen-exchange reactions between the cathodic product and the titanium oxides in the melt are possible at the cathode.

An additional reaction that takes place in a chloride bath is that between  $\text{TiO}_2$  and the chlorine liberated at the anode:



The oxygen released causes secondary oxidation of the titanium. This is why it has not yet been possible to produce the pure metal by electrolyzing titanium oxygen compounds. Usually, either comparatively pure titanium monoxide or metallic titanium with lower oxides and titanates as impurities forms at the cathode. Better results are claimed in an American patent,<sup>(4)</sup> according to which 99.9% pure titanium was obtained using a  $\text{CaO} + \text{CaCl}_2$  electrolyte (1:6) containing up to 5%  $\text{TiO}_2$  at temperatures of 700-1100°C, an anodic current density of 0.16A/cm<sup>2</sup>, and a cathodic current density of 4.5 A/cm<sup>2</sup>.

A number of measures might be projected by way of improving the electrolysis of titanium oxygen compounds. Principal among these are the following:

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Footnote (4) is on page 647.

1. Development of diagrams that resist fused titanium chlorides and chlorine.

2. Development of a process using a liquid cathode whose material would dissolve titanium but not any of the other electrolysis products. Titanium of 99.5% purity has been obtained when zinc, lead, or cadmium was used as the liquid cathode.

Currently, all cathodic deposits produced by electrolysis of titanium oxides require subsequent removal of oxygen by one method or another. For example, this might be done by electrolytic refining. As in other cases of electrolysis, that of titanium oxides requires extremely pure starting materials. Electrolysis is carried out under a current of argon or helium to protect the cathodic deposit and the electrolyte from oxidation.

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- 639 1) Patent (USA) No. 2,780,593, 1957.  
639 2) Patent (Japanese) No. 5702, 1956.  
644 3) See also patents (USA) No. 2,697,660, 1954; 2,707,168,  
1955; 2,707,169, 1955; 2,722,508, 1955; patent (British)  
No. 713,446, 1954; patent (Swedish) No. 724,198, 1955;  
745,872, 1955.  
645 4) Patent (USA) No. 3,003,934, 1961.

Chapter 25

ELECTROLYSIS OF TITANIUM WITH SOLUBLE ANODES

Electrolytic Refining of Titanium Scrap

Research on the electrolytic production of titanium in fused media with soluble anodes has been greatly expanded in recent years. Before continuing with a discussion of this research, it will be necessary to dwell briefly on the notion of the soluble anode.

Any material with the following basic properties can be used as a soluble anode [107]: electronic conductivity; the ability to react with the electrolyte without dissolving in it.

As we have already noted, titanium forms a large number of systems and compounds that exhibit these properties. The studies that have been made in the field of soluble-anode electrolysis can be classified into the following groups: electrolytic refining of titanium scrap, titanium-based alloys, and "crude anodes" - materials obtained by preliminary treatment of titanium ore concentrates with the object of endowing them with soluble-anode properties.

The production of pure, highly ductile titanium by electrolytic refining of titanium scrap is now in the industrial-testing stage.

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The basic parameters of the process and conditions for the production and storage of high-quality cathodic deposits have been determined. However, as we have noted, not all of the difficulties associated with the development of a simple, reliable, and efficient electrolyzer design have been overcome.

The common impurities that must be removed from titanium are oxygen, nitrogen, hydrogen, carbon, and iron. As a rule, the total content of these impurities is small, at 1-2% (by mass).

It has been established by numerous studies that the most suitable electrolytes for electrolytic refining are sodium chloride, either alone or mixed with potassium or strontium chloride. The former electrolyte is preferred [58, 107, 108-112].

TABLE 48  
Impurity Contents in Cathodic Deposits Obtained  
by Electrolytic Refining of Titanium

| material                 | impurity contents, % |                |                |           |           | Brinell<br>hardness | liter-<br>ature<br>source |
|--------------------------|----------------------|----------------|----------------|-----------|-----------|---------------------|---------------------------|
|                          | O <sub>2</sub>       | N <sub>2</sub> | H <sub>2</sub> | C         | Fe        |                     |                           |
| initial . . . . .        | 0.187-4.16           | 0.035-0.5      | —              | 0.31-0.78 | 0.22-0.7  | —                   | [58]                      |
| cathodic metal . . . . . | 0.027-0.004          | 0.004-0.005    | 0.0051         | 0.02-0.03 | 0.03-0.04 | 80-75               |                           |
| initial . . . . .        | 0.27                 | 0.02           | 0.016          | —         | 0.28      | 214                 | [108]                     |
| cathodic metal . . . . . | 0.01                 | 0.002          | 0.02           | —         | 0.02      | 75                  |                           |
| initial . . . . .        | 0.22                 | 0.1            | 0.012          | 0.05      | —         | 280-380             | [107]                     |
| cathodic metal . . . . . | 0.06                 | 0.001          | 0.0001         | 0.1       | —         | 100                 |                           |
| initial . . . . .        | 0.119                | 0.032          | 0.002          | 0.1       | 0.08      | 195                 | [109]                     |
| cathodic metal . . . . . | 0.024                | 0.002          | 0.002          | 0.02      | 0.01      | 80                  |                           |

Volt-ampere, chemical, and other analyses have shown that titanium goes from the anode into the melt predominantly in the form of bivalent ions in the optimum temperature range of electrolytic refining, i.e., 750-850°C. Increasing the temperature or anodic current density tends to increase the percentage of trivalent ions. The average valence of the titanium in the electrolyte is usually 2.0-2.3.

A major factor in the acquisition of high-grade deposits is the relationship between the titanium concentration in the electrolyte and cathodic current density. The optimum titanium

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concentration in the electrolyte is 3-6% (by mass). It may be assumed that the best cathodic powders are obtained at a ratio of approximately 2-3 between the electrolyte titanium concentration and the cathodic current density. The anodic current density should be 1/4-1/8 of the cathodic density in electrolytic refining.

Special attention is given the question of purifying the titanium of oxygen in research on electrolytic refining of this metal [108, 112-115]. When the process is conducted under meticulously clean conditions, the only way in which oxygen can pass from the anode to the cathode is by formation of the titanyl ion  $TiO^{2+}$ . Thermodynamic calculations indicate that formation of this ion is highly improbable up to high oxygen concentrations in the anodic material. The impossibility of oxygen transfer into the cathodic deposit in electrolytic refining of materials containing less than 1%  $O_2$  has been demonstrated with the aid of the isotope  $O^{18}$  [107, 116].

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Figure 132. Appearance of cathode with titanium deposit on it.



Figure 133. Structure of cathodic-deposit crystal.

Under the conditions described above, the product is a cathode deposit consisting for the most part of sharply outlined hexagonal or acicular crystals, whose sizes reach 15-20 mm in some cases. Figures 132 and 133

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show the external appearance of the electrolytic deposit on the cathode and an isolated crystal.

The electrolyte content in the cathodic deposit is usually 20-30% (by mass); the larger the crystals in the deposit, the smaller the amount of electrolyte left in it. The current efficiency is 70-90% for the discharge of  $Ti^{2+}$ .

Table 48 lists data on the purity of titanium obtained at the cathode in electrolytic refining.

No more than 4-5 kW·h of electric power is used per kilogram of titanium directly in the electrolysis process. The total electric power consumption ranges up to 10-11 kW·h/kg.

#### Electrolytic Refining of Alloys

Electrolytic refining of titanium-based alloys is a more difficult problem than electrolytic refining of contaminated titanium. This process may take either of two directions:

1. Separation of the titanium from the other alloy components [52, page 91; 107-109; 118-119].
2. Removal of nonmetallic components from the alloy [106, page 213].<sup>(1)</sup>

The first approach assumes subsequent regeneration of the anodic-sludge components. The second is simpler, but requires separate storage of the scrap and its classification.

Alloys are usually refined under the same process conditions as titanium scrap. The principal electrolyte used is NaCl. The titanium ion concentration in the electrolyte is 1-5% (by mass). The ordinary anodic current densities range from 0.2 to 0.4 A/cm<sup>2</sup>. Temperature varies from 800 to 850°C. During the initial stages of refining of Ti-Al alloys, titanium containing hundredths of a percent of aluminum is at first deposited on the cathode, but then aluminum content in the cathode deposits increases rapidly. Alloys with chromium and vanadium behave similarly. Manganese begins to deposit on the cathode in the very first stages of

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Footnote (1) is on page 661.

TABLE 49

Results of Experiments in Electrolytic Refining of Binary Alloys

| initial anodic material | element  | cathode deposit | anodic sludge |              |             | elec-trolyte          | distil-lation |
|-------------------------|----------|-----------------|---------------|--------------|-------------|-----------------------|---------------|
|                         |          |                 | outer layer   | middle layer | inner layer |                       |               |
|                         |          |                 |               |              |             |                       |               |
| Ti+1% Fe                | titanium | 99.6            | 80.0          | 77.9         | 78.0        | 0.4<br>none<br>found  | none<br>found |
|                         | iron     | 0.2             | 19.7          | 20.3         | 22.0        |                       |               |
| Ti+5% Fe                | titanium | 99.7            | --            | 53.8         | --          | 0.55<br>none<br>found | none<br>found |
|                         | iron     | 0.3             | --            | 41.3         | --          |                       |               |
| Ti+10% Fe               | titanium | 96-100          | 58.0          | 58.7         | 59.5        | 1.0<br>0.2            | none<br>found |
|                         | iron     | 0.2             | 40.8          | 41.0         | 40.4        |                       |               |
| Ti+20% Fe               | titanium | 93.3            | --            | 54.8         | --          | 0.7<br>traces         | --<br>traces  |
|                         | iron     | 0.6             | --            | 54.0         | --          |                       |               |
| Ti+1% Si                | titanium | 99.33           | 87.0          | 86.0         | 89.5        | 0.4<br>none<br>found  | --<br>traces  |
|                         | silicon  | traces          | 12.5          | 13.7         | 10.6        |                       |               |
| Ti+5% Si                | titanium | 99.4            | 79.0          | 79.0         | 79.5        | 0.5<br>none<br>found  | --<br>traces  |
|                         | silicon  | traces          | 20.0          | 21.0         | 19.6        |                       |               |
| Ti+10% Si               | titanium | 99.0            | 78.0          | 78.0         | 78.0        | 1.0<br>none<br>found  | --<br>traces  |
|                         | silicon  | none<br>found   | 22.2          | 21.8         | 21.4        |                       |               |
| Ti+5% Nb                | titanium | 99.0            | --            | 84.0         | --          | 1.0<br>traces         | none<br>found |
|                         | niobium  | none<br>found   | --            | 15.1         | --          |                       |               |
| Ti+10% Nb               | titanium | 98.5-99.0       | 54.2          | 53.3         | 56.2        | 0.3<br>none<br>found  | none<br>found |
|                         | niobium  | none<br>found   | 46.0          | 45.7         | 42.0        |                       |               |
| Ti+20% Nb               | titanium | 97.6            | --            | 35.4         | --          | 1.0<br>none<br>found  | none<br>found |
|                         | niobium  | 0.18            | --            | 63.0         | --          |                       |               |
| Ti+1% Al                | titanium | 97.3            | 89.0          | 87.8         | 89.9        | 0.5<br>0.2            | --<br>traces  |
|                         | aluminum | 0.36            | 10.6          | 9.9          | 9.8         |                       |               |
| Ti+5% Al                | titanium | 97.3            | 79.0          | 78.5         | --          | 0.6<br>0.4            | --<br>traces  |
|                         | aluminum | 1.52            | 19.5          | 21.0         | --          |                       |               |
| Ti+10% Al               | titanium | 92.2            | 50.0          | 56.0         | 69.5        | 0.3<br>0.2            | none<br>found |
|                         | aluminum | 7.3             | 50.0          | 42.2         | 30.4        |                       |               |

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electrolysis in amounts that exceed its content in the original anode. Good removal of Fe, Cu, Mo, Si, N<sub>2</sub>, C, and O<sub>2</sub> from the titanium has been reported.

Certain problems in the electrolytic refining of a series of binary titanium-based alloys are discussed in [118]. A mixture of potassium and sodium chlorides (1:1 by mass) was used for the refining process. The process temperature was 760-800°C. The anodic material was depleted to a depth of 5-10 mm. The results of these experiments are assembled in Table 49.

Analysis of the results of these experiments leads us to the following conclusions: firstly, electrolysis of titanium-iron, titanium-silicon, and titanium-niobium alloys separates the components well; secondly, the proportions between the components in all layers of the anodic sludge remains approximately constant after a certain anode-depletion depth has been reached, and, thirdly, the composition of the anodic sludge depends only on the initial proportions of the components in the alloy right up to the point at which the first intermetallic compounds are formed. These last two circumstances suggest that diffusion processes in the original alloy are not a major factor in electrolysis. The process mechanism consists in release of the titanium from the first superficial layer into the melt for each initial anodic-material composition, a process that continues until its potential is so high that liberation of titanium from this layer ceases and the next layer of the original composition begins to dissolve, and so forth; simultaneous solution of titanium from two successive layers and diffusion of titanium from one layer to another are improbable.

Below we present equilibrium-potential values for titanium and metals commonly encountered as components of titanium-based alloys. The figures pertain to chloride electrolytes, near-unity activities of the corresponding metal ions in the melt, and temperatures of 850-900°C [65, 76]:

| <u>Anodic reaction</u>        | <u>-E, V</u> | <u>Anodic reaction</u>        | <u>-E, V</u> |
|-------------------------------|--------------|-------------------------------|--------------|
| Mn/Mn <sup>2+</sup> . . . . . | 1.967        | Al/Al <sup>3+</sup> . . . . . | 1.55         |
| Mn/Mn <sup>2+</sup> . . . . . | 1.766        | Al/Al <sup>3+</sup> . . . . . | 1.4          |

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Alloys

| <u>Anodic reaction</u>        | <u>-E, V</u> | <u>Anodic reaction</u>        | <u>-E, V</u> |
|-------------------------------|--------------|-------------------------------|--------------|
| Ti/Ti <sup>2+</sup> . . . . . | 1.826        | V/V <sup>2+</sup> . . . . .   | 1.5          |
| Ti/Ti <sup>3+</sup> . . . . . | 1.793        | Fe/Fe <sup>2+</sup> . . . . . | 1.293        |
| Cr/Cr <sup>2+</sup> . . . . . | 1.523        | Si/Si <sup>4+</sup> . . . . . | 1.28         |
| Cr/Cr <sup>3+</sup> . . . . . | 1.307        | Nb/Nb <sup>3+</sup> . . . . . | 1.1 - 1.2    |

These data suggest the possibility of separating titanium from most of these metals (except Mn) under nearly reversible conditions. When we consider that the usual content of a given single impurity in titanium varies from 1 to 10%, this possibilities even further enhanced. However, application of an electric current causes considerable polarization, which is determined basically by the titanium-ion concentration gradient in the pores of the steadily growing sludge layer as titanium is depleted from the anodic material. The decrease in titanium concentration in the surface layers of the anode and shielding of the anode surface by the sludge layer are also of some importance here. At certain degrees of anode depletion, therefore, more electropositive impurities begin to dissolve in the electrolyte along with the titanium and settle on the cathode. The extent to which the titanium is separated from these impurities can be increased by lowering the anodic current density, accelerating diffusion processes in the sludge-layer pores, removal of this layer, work with bipolar electrodes, changing electrolyte composition, and a number of other measures.

In considering the electrolysis of binary and other alloys, it is necessary to remember that the alloy components may influence one another strongly and that third components are also important. Here we refer not to the appearance of new phases, which is also possible, but to the fact that even very small additives of third components may change the potential of the principal component in the alloy.

Major factors in the electrolytic refining of alloys are complexing in the melts, the volatilities of the chlorides that are formed, the surface-energy change of the anode as it dissolves, and a number of other circumstances.

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### Electrolytic Refining with Crude Anodes

An extremely interesting but rather neglected process is that of electrolytic refining of crude anodes. There are many methods for converting ores and ore concentrates to a state in which they can be used as soluble anodes. Among these methods, the following deserve mention:

1. Reduction of the raw material, complete or partial;
2. Nitridizing of the raw material;
3. Carbiding of the raw material.

Reducing agents used include: carbon [55, 123],<sup>(2)</sup> magnesium [58],<sup>(3)</sup> aluminum [58],<sup>(4)</sup> and calcium hydride or calcium [118], which are the strongest reducing agents, as well as other elements and compounds. The reduction process is run either in steps, with formation of titanium monoxide in the first stage and conversion of a number of other components to the metallic state with the object of subsequent separation, or straight through to the conversion of all raw-material components to the metallic state and formation of an alloy suitable for electrolytic refining. The latter process is preferred at present.

The reduction of ilmenite slags and titanium concentrates of the compositions indicated in Table 50 was investigated in [118].

TABLE 50  
Chemical Compositions of Ilmenite Concentrates and Slags Used for Reduction by Calcium Hydride

| material    | contents of components, % (by mass) |                  |                                |                                |       |     |         |              |
|-------------|-------------------------------------|------------------|--------------------------------|--------------------------------|-------|-----|---------|--------------|
|             | TiO <sub>2</sub>                    | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO   | MnO | MgO     | other oxides |
| slag        | 85.0                                | 1.65             | 10.5                           | 0.7                            | 0.8   | 1.8 | 5.35    | 2.0-3.0      |
| concentrate | 48.0-50.0                           | 2.65             | 1.5-2.5                        | 4.0-6.0                        | 34-38 | 1.0 | 0.8-1.5 | 4.0-5.0      |

The reduction was carried out in closed stainless-steel containers. The reducing agent was calcium hydride. The following optimum reduction conditions were established:

Footnotes (2), (3) and (4) are on page 661.

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a) for slag: temperature 1100°C, time 2 hours, calcium hydride consumption 1.8-2.0 kg/kg of Ti;

b) for concentrate: temperature 1200°C, time 2 hours, calcium hydride consumption 2.2-2.4 kg/kg of Ti.

The result was extraction of 85-95% of the Ti in the form of the solid solutions whose compositions are given in Table 51.

TABLE 51  
Chemical Compositions of Products Obtained After Reduction of Titanium Concentrates and Slags with Calcium Hydride

| reduction product     | contents of components, % (by mass) |      |      |      |      |            |         |
|-----------------------|-------------------------------------|------|------|------|------|------------|---------|
|                       | Ti                                  | Si   | Al   | Fe   | Ca   | Mn         | other   |
| slag . . . . .        | 86,5                                | 0,35 | 6,0  | 0,61 | 0,25 | none found | 5,0-6,0 |
| concentrate . . . . . | 88,5                                | 1,0  | 0,32 | 0,45 | 0,05 | 0,20       | 8,0-9,0 |

Electrolytic refining of these materials under conditions similar to those of electrolytic titanium-alloy refining produced cathodic deposits containing 99.6% Ti, 0.05% Si, 0.07% Al, 0.2% Fe, 0.04% Mn, the hardness of the metal was ~100 HB.

Comparatively pure titanium nitride and carbide can be produced by nitridizing and carburizing the raw material with subsequent concentration of the product.

TABLE 52  
Temperature Conditions of Nitridizing Process and Stability of the Nitrides

| Nitridizing process                               | Process temp. °C | Nitride decomposition temp. °C | Substance decomposing the nitride |
|---|------------------|--------------------------------|-----------------------------------|
| FeO → Fe <sub>3</sub> N                           | 450-670          | >670                           | —                                 |
| MnO → Mn <sub>3</sub> N <sub>2</sub>              | 1000-1100        | >1100                          | —                                 |
| MgO → Mg <sub>3</sub> N <sub>2</sub>              | >900             | —                              | —                                 |
| TiO <sub>2</sub> → TiN                            | 1250             | 1800                           | Cold water                        |
| Al <sub>2</sub> O <sub>3</sub> → AlN              | VV 1500          | 1750                           | steam at 500°C                    |
| CaO → Ca <sub>3</sub> N <sub>2</sub>              | VV 1800          | —                              | Cold water                        |
| SiO <sub>2</sub> → Si <sub>3</sub> N <sub>4</sub> | V 1600           | —                              | —                                 |
| SiO <sub>2</sub> → Si <sub>3</sub> N <sub>4</sub> | V 1400           | —                              | Highly stable                     |

The temperature ranges of nitridizing and the stabilities of the nitrides obtained from the oxides in slags of the compositions given in Table 50 are given in Table 52 (nitridizing was

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carried out with nitrogen in the presence of carbon).

Three groups of substances are obtained by nitriding in the 1250-1300°C temperature range:

1. Metals (iron, manganese).
2. Metal nitrides (titanium and magnesium nitrides).
3. Metal oxides.

The resulting multiphase system is separated comparatively easily by clarification and treatment with nitric acid. The result is a material that contains up to 90% titanium nitride and whose composition renders it suitable for use as a soluble anode. Electrolytic refining of this material produced a cathodic metal containing 98-99% Ti; it could be converted into high-grade metal by secondary refining.

A considerable amount of work has now been done on the electrolytic refining of titanium nitrides, carbides, oxycarbides, oxycarbonitrides, and lower oxides of titanium obtained for ores and prepared synthetically [56, 57, 59, 107, 118, 121-125].<sup>(5)</sup>

Hickman and Willes [124] found that the best material for electrolytic refining is a carbide containing 11-13% C. Their work was done with the following electrolysis parameters: electrolyte composition, an equimolar mixture of potassium and sodium chlorides with a small lithium-chloride additive; titanium dichloride concentration, 2-3.5%; temperature, 675-750°C. The product was highly purified titanium with a hardness of 90-110 HB units.

An American patent<sup>(6)</sup> gives the following conditions and results for electrolytic refining of titanium carbide that had first been briquetted with pitch and coked at 1000°C for 2 hours. Initial carbides: ~69% Ti, 31.0% C, 0.12% Fe, 79.2% Ti, 20.2% Fe. Electrolysis temperature 850°C, anodic current density 0.23-0.3 A/cm<sup>2</sup>, cathodic density 2.1-2.4 A/cm<sup>2</sup>. Titanium extraction 72-75% in the best experiments; hardness 196 HB.

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Footnotes (5) and (6) are on page 661.

TABLE 53  
Process Data for Titanium Carbide Electrolysis

| content in anode, %                        |    |        | electrolyte composition                | cathodic current density, A/cm <sup>2</sup> | current efficiency, % | impurity contents in cathodic metal, % |      |      | No  |
|--|----|--------|--|---|-----------------------|--|------|------|-----|
| Ti   | C  | N      |  |   |                       | N                                      | C    | O    |     |
| primary carbide                            |    |        |  |   |                       |  |      |      |     |
| 66   | 24 | 0.13   | LiCl + KCl                             | 2.5   | 85                    | 0.3                                    | 0.4  | 0.3  | 210 |
| 68   | 21 | 0.15   | NaCl + TiCl <sub>4</sub>               | 2.5   | 85                    | 0.5                                    | 0.5  | 0.5  | 220 |
| 70   | 27 | 0.6    | NaCl + K <sub>2</sub> TiF <sub>6</sub> | 2.5   | 85                    | 0.6                                    | 0.02 | 0.14 | 175 |
| 67   | 21 | 0.1    | NaCl + K <sub>2</sub> TiF <sub>6</sub> | 2.5   | 85                    | 0.1                                    | 0.3  | 0.3  | 220 |
| 79   | 20 | 0.08   | NaCl + K <sub>2</sub> TiF <sub>6</sub> | 2.5   | 85                    | 0.1                                    | 0.05 | 0.12 | 187 |
| cathodic metal after electrolytic refining |    |        |  |   |                       |  |      |      |     |
| 80   | 40 | 120.1  | NaCl + TiCl <sub>4</sub>               | 1.5   | 130                   | 0.03                                   | 0.03 | 0.12 | 120 |
| 80   | 10 | 0.20.7 | NaCl + K <sub>2</sub> TiF <sub>6</sub> | 1.0   | 105                   | 0.00                                   | 0.00 | 0.11 | 105 |

\*Calculated for trivalent titanium.

The authors of [121] refined porous sintered TiC briquettes in various electrolytes (chloride and chloride-fluoride) at 850°C. The electrolyte contained from 3 to 5% of titanium ions. It was shown that the titanium is released from the anode predominantly in the form of trivalent ions. The authors subjected the product obtained by the TiC electrolysis to secondary refining. The results of these experiments are given in Table 53.

Electrolytic refining of titanium nitride must be carried out in a current of inert gas to remove the nitrogen; as a result, titanium nitrides containing more nitrogen than the mononitride do not form under the conditions of electrolysis, and the nitrogen is evolved into the gaseous phase as the titanium dissolves. In the best experiments, metal containing 0.03% of N<sub>2</sub> was obtained by a single electrolytic refining of synthetic titanium nitride [118].

Several stages are required for the electrolytic refining of titanium monoxide. In the first stage, refining produces titanium sesquioxide Ti<sub>2</sub>O<sub>3</sub> at the anode. When all of the titanium

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monoxide has been converted into this product, it begins to refine electrolytically, with formation of almost stoichiometric titanium dioxide at the anode. The cathodic metal then contains 0.2-0.3% of  $O_2$ .

The electrolytic refining of titanium nitrides, carbides, and monoxide proceeds at voltages somewhat higher (by 0.5-0.8 V) than the refining of titanium scrap. Good refining is obtained in a sodium-chloride or mixed sodium-potassium-chloride melt. The anodic current densities should not exceed 0.2-0.5 A/cm<sup>2</sup>; at higher current densities, titanium tetrachloride is formed and evolved from the electrolyzer in the form of puffs of white smoke.

#### Processing the Cathode Deposits

Electrolysis results in titanium crystals that are usually strongly bonded to the cathode and to one another and are to some degree cemented together by salts. This material must be separated after extraction from the electrolyzer. There are now two basic methods - hydrometallurgical and distillation - for separating the salt and the metallic deposit.

In the former method, the cathodic deposit is crushed and ground and then treated with dilute (0.5-1%) hydrochloric acid solution. Three such treatments are the optimum, with an overall liquid:solid ratio ranging from 9 to 12 (depending on the proportions of salt and metal in the deposit). The hydrochloric-acid treatment is followed by water washing, which can be carried out either in mixers or directly on the filters. Treatment with water on the filters is broken off when no more chlorine ion can be detected in the filtrate; then the material is washed with a drying reagent (e.g., ethyl alcohol) and dried in vacuum drying cabinets at 50-60°C.

If the cathode deposit contains large amounts of electrolyte (50% or more), it is advisable to melt the electrolyte out of the deposit prior to hydrometallurgical treatment or (after crushing and grinding) to separate the salt and metal in a current of nitrogen, an operation for which any aeration equipment

can be used. This reduces substantially the amount of hydrochloric acid that must be used to wash the deposits.

The salt is separated from the metal by distillation under conditions and in apparatus similar to those used to purify metallothermic reaction mass.

The hydrometallurgical treatment is more advantageous for a coarse-grained titanium deposit.

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### Footnotes

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- 651 1) See also patents (USA) No. 2,920,022, 1960;  
2,913,380, 1959.
- 655 2) Patents (USA) No. 2,917,440, 1959; 2,813,069, 1957.
- 655 3) See also patents (USA) No. 2,904,428, 1959; 2,909,473,  
1959.
- 655 4) Patent (Japanese) No. 3705, 1957.
- 657 5) See also patents (British) No. 791,151, 1958; 791,153,  
1958; 792,716, 1958; 778,218, 1957; 786,460, 1957; pat-  
ent (USA) No. 2,851,030, 1958.
- 657 6) Patent (USA) No. 2,920,021, 1960.

Symbol List

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## Chapter 26

### ELECTROLYZERS FOR PRODUCTION AND REFINING OF TITANIUM

The process in which titanium is produced by electrolysis of fused media has a number of peculiarities, which impose certain requirements on electrolyzer designs. Principal among these are the following:

1. Because of the high reactivity of titanium and its compounds of lower valence, electrolysis must be conducted in equipment that works in an inert-gas atmosphere.
2. The aggressiveness of the lower titanium chlorides and fluorides with respect to a broad range of materials makes it necessary to use structural materials that are highly resistant to corrosion and difficult to reduce.
3. High-quality titanium crystals form in a relatively narrow range of ratios of titanium concentration in the electrolyte to cathodic current density.

These factors and a number of others make it necessary to conduct the electrolysis under conditions such that the process becomes nearly continuous.

Insoluble-anode work involves a number of specific difficulties and disadvantages:

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1. Electrolysis of chlorides and fluorides proceeds with liberation of chlorine; this necessitates thorough protection not only of the parts of the equipment that come into contact with the electrolyte, but also those situated above it.

2. The evolution of chlorine or chlorocarbons increases the danger of secondary oxidation or chlorination of the cathodic deposits and the lower titanium chlorides present in the melt. The process must be carried out at relatively low volume current densities.

3. Insoluble-anode electrolysis requires a higher voltage on the electrolyzer's terminals.

The soluble-anode process can be conducted at very low electrolyzer terminal voltages and without the evolution of chlorine at the anode. High volume current densities are used, so that the work can be done in small baths. However, this process is characterized by a specific difficulty consisting in the need to replace the anodic material.

Special difficulties are encountered in the storage, purification, and transfer of the electrolyte, for which special equipment is required.

These basic peculiarities and difficulties of electrolysis technology must be taken into account in selecting electrolyzer designs.

Bath material and lining. Numerous studies concerned with selection of bath materials and linings for work with insoluble anodes indicated that it is advisable to use stainless steel for the shell of the bath; its inner surface is protected with dense graphite or by creating a slag lining of electrolyte on the cooled walls of the bath. The conditions under which the liner is formed are selected individually for each bath. This gives rise to another difficulty: control of temperature inside the bath. It has been reported that type 18/8 steel with 5% Mo may be quite stable in insoluble-anode work [41]. However, use of this material will require additional research. In rare cases, electrolyzers are lined with some of the most stable ceramic materials.

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Type 18/8 steel can be used as a bath material in soluble-anode work. A pressure-tight bath made from this material may last for up to one year.

Bath shape. This is determined basically by the shape of the cathode. Circular-section baths may be regarded as the simplest and more convenient types for electrolyzers working with currents up to 10 kA. However, use of rectangular-section baths is not excluded for specific cathode types. Bath dimensions are determined on the one hand by the design features of the bath (method of extracting the cathode deposit, etc.) and, on the other, by technological parameters, chiefly current density.

It may be assumed as a first approximation that an anodic current density of 0.1-0.4 A/cm<sup>2</sup> is adequate for soluble-anode work.

Mutual positioning and shape of electrodes. The influence of the relative positions of the electrodes on the course and stability of the electrolysis process and the quality of the cathode deposits has been determined as a result of numerous experiments. Various electrode shapes that were acceptable from the standpoint of design convenience and optimum retention of the electrolytic deposits on the cathodes were investigated. Some of the simplest electrode position and shape options are represented schematically in Fig. 134.

Practical experience has shown that if the optimum electrolysis conditions are observed, it becomes unnecessary to use shaped cathodes, since the cathode deposits are bonded strongly to smooth electrodes. During electrolysis (especially with soluble anodes), an effort must always be made to obtain the most uniform distribution of the electric field over the surface of the electrode and to enclose the cathode in the anode to the extent possible, since higher cathodic current densities require heavy ion influxes.

Thus, it can be stated that the electrode shapes and positions shown in Fig. 134, c, f, and g, will be most efficient.

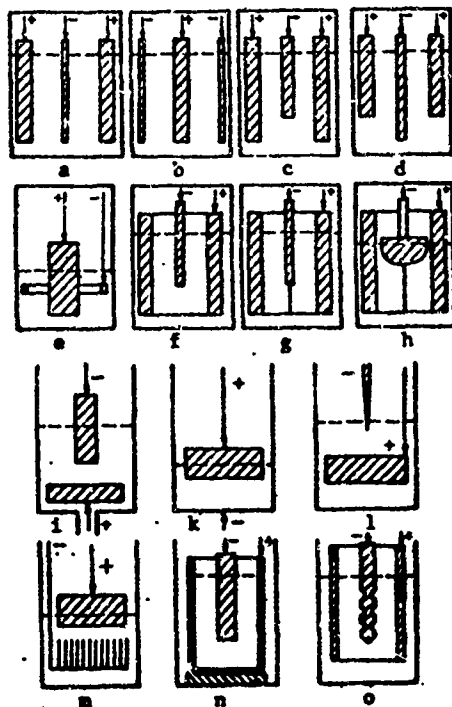


Fig. 134. Electrode shapes and relative positions. a) plate anode, plate or rod cathode, square-section bath; b) plate anode, plate cathode, square-section bath; c) plate anode, plate or rod cathode, square-section bath; d) plate anode, plate or rod cathode, square-section bath; e) cylindrical anode, annular cathode, circular-section bath; f) hollow-cylinder anode, rod cathode, round- or square-section bath; g) hexagonal anode, rod cathode, circular- or square-section bath; h) hexagonal anode, spherical cathode, circular- or square-section bath; i) anode at bottom, cathode at top; k) container-type cathode; l) needle cathode, circular-section bath; m) comb cathode; n) cup anode; o) hollow-cylinder anode, shaped cathode.

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Figure 134 indicates electrode relative positions for compact anodes. However, blocks of pressed metal (rods, plates) and loose material (sponge, fragments, briquettes), which are placed in perforated baskets made from iron, graphite or nickel, may also be used as soluble anodes. A very wide variety of relative electrode arrangements may be used in work with insoluble anodes.

Delivery of material into electrolyzer. Delivery of the material for electrolysis is comparatively simple in insoluble-anode work. The carbon tetrachloride is fed directly into the bath through pipes. Lower titanium chlorides can be poured into the melt together with the alkali- or alkaline-earth chlorides from the container in which the electrolyte is prepared in advance and stored.

It is convenient to load solid titanium oxides and hexafluorotitanate into the electrolyzer both at the beginning of electrolysis and during the process, using hermetic feeders; the same applies for the case of loose solid anodes.

Work with compact soluble anodes requires special devices for their introduction into the electrolyzer and extraction of the depleted material. The anode may be either endless (ribbon, rod) or handled with various types of special clamping mechanisms. Extraction of the anodic sludge is a difficult problem in electrolysis with bulk soluble anodes.

Unloading the cathodic product. It is most desirable to produce cathodic deposits that are quite strongly bound to the cathode, since these deposits may be contaminated by the anodic sludge if they drop off the electrode of themselves; additional metal losses are also possible. A deposit bound to the cathode can be unloaded either by dropping it into special hoppers (using cutting devices or vibrators) or by changing cathodes during electrolysis.

Some of the methods used to unload the cathodic product are illustrated schematically in Fig. 135.

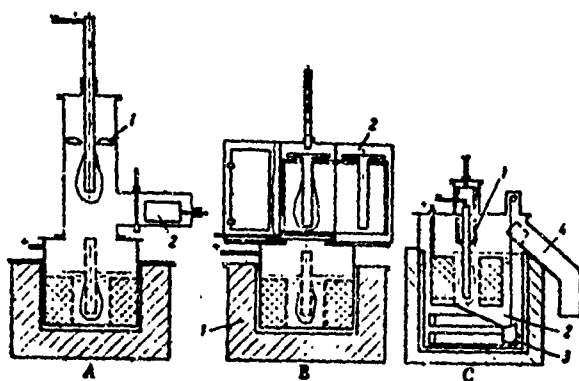


Figure 135. Schematic diagrams showing removal of cathode deposit from electrolyzer. a) Cathode deposit cut off inside electrolyzer by knives 1 and removed with air-lock receiver 2; b) cathode sealed off from electrolyzer 1 and chamber 2, which is filled with inert gas or evacuated; c) cathodic deposit cut off by knives 1 in melt 2 and removed from electrolyzer with receiver 3 and lock 4.

Temperature control. Experiments have shown that temperature may be self-regulating in the electrolytic process. However, furnaces or electrode heaters are necessary to preheat the bath and maintain temperature with minimum expenditure of direct current. Resistance and gas-fired furnaces can be used.

Stabilization of concentration in the cathode layer of electrolyte. In soluble-anode work, concentration is stabilized in the electrolyte basically by adjusting the distance between the electrodes and their relative positions. In work with insoluble anodes, concentration is maintained by regular infeed of material.

Method of establishing contact between current lead-ins and electrodes. This question is of particular importance in view of the fact that the electrodes must be moved during the process (clipping the cathode deposit, extracting cathodes, etc.). There are two possible approaches. In the first, flexible current leads (ribbons, woven straps, etc.) are permanently connected, while the second uses liquid contacts through molten metals and alloys

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Both contacting methods have acquitted themselves well; either may therefore be selected on the basis of the electrolyzer's design features. In most cases, the anode voltage can be applied to the shell of the bath.

Process control. A single thermocouple and temperature controller are adequate for temperature control. The most important control needed in the electrolysis process is measurement of the concentration of the titanium-containing compound in the electrolyte. This can be done by tapping during the process for chemical analysis or, in the case of a stable process, by measuring back emf's, which reflect quite accurately any concentration changes that take place in the bath.

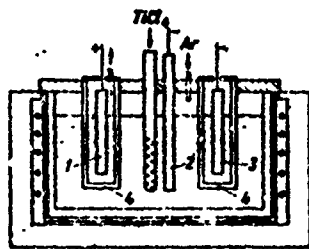


Figure 136. Electrolyzer for production of titanium from  $TiCl_4$ .

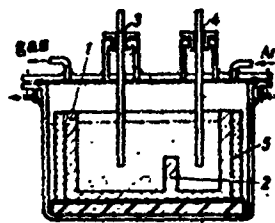


Figure 137. Electrolyzer for production of titanium from its oxides.

Monitoring of the inert-gas pressure in the electrolyzer is mandatory to prevent penetration of air into it and to secure the process. Electrolyte level changes during electrolysis, and this requires periodic replenishment and, consequently, devices for monitoring electrolyte level.

When titanium tetrachloride is used, special devices must be provided to monitor its flow rate.

Many different bath designs have now been proposed. Some of them are laboratory types, some have been built as semi-industrial installations, and some have been designed as industrial versions. Schematic diagrams of intermittent-type electrolyzer designs are

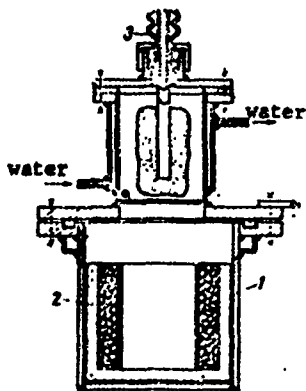


Figure 138. Laboratory electrolyzer for production of titanium from soluble anodes.

Titanium oxides are electrolyzed in the second electrolyzer (Fig. 137). Bath 1 is made of graphite and has a graphite partition 2. Loose titanium dioxide is placed on the floor of the bath on one side of the partition, and anode 3 is introduced through hermetically sealed plug into the electrolyte above it. Cathode 4 is introduced into the cathode space. The bath is heated by heating elements 5.

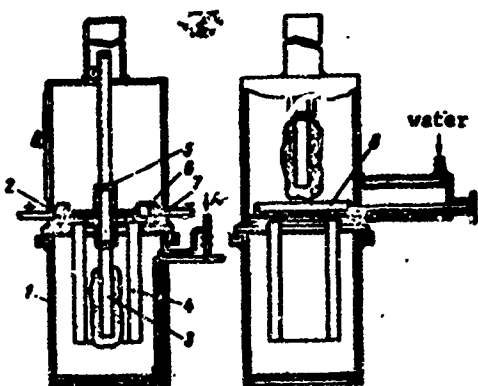


Figure 139. Electrolyzer for production of titanium from soluble anodes at 5000 A.

given in Figs. 136-138.

The first design (Fig. 136) is intended for electrolysis of lower titanium chlorides. It consists of a ceramic bath that receives anode 1, which is surrounded by ceramic diaphragm 4, and two cathodes - cathode 2 for preliminary reduction of  $TiCl_4$ , which is enclosed in diaphragm 4, and cathode 3, on which electrolytic titanium powder is formed.

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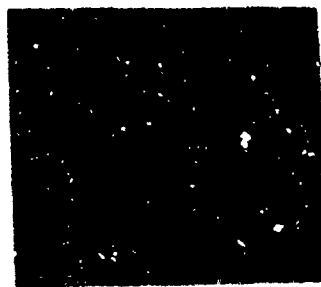


Figure 140. 10,000-ampere electrolyzer for production of titanium from soluble anodes.

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Figure 141. External appearance of 5000-ampere electrolyzer.



Figure 142. External appearance of 10,000-ampere electrolyzer.

The third electrolyzer (Fig. 138) is designed for electrolysis with soluble anodes. A perforated cylinder or cup 2 is placed in graphite cup 1, which serves as the anode. The material to be electrolytically refined is sprinkled into the space between the cylinder walls and the graphite cup. Cathode 3 is introduced into the perforated cylinder.

All three types of electrolyzers are enclosed in hermetically sealable metal cases with pressure-tight covers and packed entrances for the electrodes.

Figures 139-142 show diagrams and photographs of intermittent semi-industrial electrolyzers for work with soluble anodes.

The first electrolyzer (Fig. 139) consists of stainless-steel bath 1 and cover 2, which seals it hermetically. Cover 2 has holes at the bottom for insertion of anode 4 and cathode 3. Two dishes, 6 and 7, which are filled with soft solder and connected to the dc source, are placed on the floor of the cover, which is lined with asbestos cement. Anodes 4 in the form of compact specimens or loose material between the walls of a cylindrical perforated basket are passed through the hole in the base of cover 2.

Cathode 3 is fitted with a plate that covers the hole in the bottom of cover 2. The shank of blade 5, which is used to cut off the cathode deposit, passes through a hole in this plate.

The anode and cathode have lugs that fit into dishes 6 and 7. A container with a sliding floor for collection of the cathode deposit is fitted at the side of cover 2. As the cathode is lifted, cutter 5 bears against the top of cover 2 and shears off the deposit, which drops onto sliding floor 8. The work of the bath is done when all of the anode material has been depleted. The electrolyte is then displaced by argon pressure through the drainpipe into an auxiliary container and the electrolyzer is reloaded. This electrolyzer works with 5000 amperes of current.

The second electrolyzer (Fig. 140), a 11,000-A version, is based on low-carbon-steel tank 1, which is enclosed in liner 2 [109]. Two water-cooled cylindrical cathode chambers 3, each with two cam-type vacuum slides, two anode chambers 4 with cam slides and hoppers, and a central chamber for introduction of the heater are welded into the top of the tank.

The bath heater consists of a steel spiral and four steel electrodes.

Before starting work, the bath is filled with the anodic material and granulated sodium chloride through the central hole; then the heater is bolted on, a certain part of the electrolyte is premelted with the steel starter spiral, and melting is completed with the electrodes. Temperature is controlled by raising and lowering the electrodes. After melting and cooling, lump electrolyte ( $\text{NaCl} + \text{TiCl}_2$ ) is added to the bath and the melting process is repeated.

Then the cathode-chamber slides are opened, the cathode is lowered into the bath, and the negative terminal is connected to it. The positive terminal is connected directly to the tank. During electrolysis, the lower vacuum slide covers almost the entire cross section of the cathode chamber.

During the work, anodic material and electrolyte are fed into the bath through the previously evacuated and helium-filled anode-chamber hoppers with the vacuum slide open.

The cathode deposits are extracted into the cathode chamber and cut off the cathode with a cylindrical cutter.

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7. Work on the design and construction of various electrolyzer designs is continuing without letup. The proposed electrolyzers include highly original models. One American patent<sup>(1)</sup> describes an electrolyzer that works at temperatures  $>1600^{\circ}\text{C}$  to produce molten titanium; the author of [91]<sup>(2)</sup> proposes a continuously extracted cathode on which a semisintered deposit of metallic titanium is formed at very high current densities. An interesting electrolyzer is proposed in the British patent.<sup>(2)</sup> The electrolyzer consists of three compartments separated by walls that do not reach up to the surface of the anode. The anode is a fused metal (Sn, Pb, etc.), which circulates through all compartments. Scrap is loaded into the anode in the first compartment; an auxiliary cathode is also used here to collect impurities. Pure titanium is deposited on the working cathode in the second compartment. The third compartment serves for removal of sludge.

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Footnotes (1) and (2) are on page 674.

Footnotes

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1) Patent (USA) No. 2,917,440, 1959; 2,887,443, 1959.

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2) Patent (British) No. 847,878, 1960.

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Part VIII

PRODUCTION OF TITANIUM DIOXIDE

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## Chapter 27

### DEVELOPMENT OF TITANIUM DIOXIDE PRODUCTION AND ITS PROPERTIES

The chloride metallurgy that made it possible to produce titanium tetrachloride after dressing titanium-containing raw materials has opened broad prospects for large-scale industrial production not only of metallic titanium, but also of titanium dioxide, production of which has been developing rapidly in recent years

The production of pigment titanium dioxide in the capitalist countries, which was only about 1 thousand tons per year in 1920, had increased to about 10 thousand tons by 1930 and reached 102 thousand tons in 1939 [1].

The influx of investment into the production of titanium dioxide, which stopped temporarily during the Second World War, resumed at the end of the war and grew to substantial dimensions. In 1962, the capacity of the capitalist countries to produce titanium dioxide was estimated at about 1100 thousand tons, and more than half of it was American capacity [1]. The actual amounts of titanium dioxide produced in the USA during recent years have been as follows: 413 thousand tons in 1960, 456 thousand tons in 1961, about 479 thousand tons in 1962 and 1963, 508 thousand tons in 1964, and 520 thousand tons in 1965. The expected 1966 production of titanium dioxide in the USA is 585 thousand tons [2, 3].

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Substantial further expansion of titanium dioxide production capacity has been reported; the figure for the capitalist world is put at about 1.5 million tons per year. The production capacity of the USA, which was 420 thousand tons in 1957, had risen to 640 thousand tons in 1962 [4], and it was estimated at about 700 thousand tons in mid-1963, i.e., it had already reached the level that American experts had predicted only for 1970 [2].

The Japanese are also giving a great deal of attention to the development of titanium dioxide production capacity. The total productive capacity of Japanese firms, which was 61 thousand tons at the end of 1960, was to increase to 113 thousand tons in 1965 [5].

TABLE 54  
Principal Producers of Titanium Dioxide in  
the Capitalist Countries [1]

| Firm                           | Countries in which the firm's plants are located            | Capacity at end of 1961, thousands of tons per year |
|--------------------------------|---|---|
| National Lead                  | USA, Canada, West Germany, Belgium                          | 379   |
| Dupont de Nemours              | USA, Mexico   | 168   |
| British Titan Products         | England, Australia, UAR; plant under construction in Canada | 130   |
| American Cyanamid              | USA   | 81  |
| Farbenfabriken Bayer           | West Germany  | 61  |
| Glidden                        | USA   | 51  |
| New Jersey Zinc                | USA   | 44  |
| Laporte                        | England; under construction in Australia                    | 41  |
| Montecatini                    | Italy   | 41  |
| Isihara                        | Japan   | 37  |
| deThann et de Mulhouse, et al. | France  | 31  |
| Vuorikelana                    | Finland   | 16  |
| Other firms                    | Western Europe, Japan, India, USA, Canada, Latin America    | 53  |
|                                | TOTAL   | 1133  |

The total production capacity of French plants for titanium dioxide, which was 31 thousand tons at the end of 1961 [1], had increased by 18 thousand tons by the end of 1962;  $TiO_2$  production capacity was to be doubled in this country during the next few

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years [6].

A number of titanium dioxide production plants have been built or planned in recent years in West Germany and other countries of western Europe, as well as in Canada, Argentina, and certain Asian and African countries [5-13].

Most of the titanium dioxide production capacity of the capitalist world is concentrated in the hands of a small number of giant monopolies (Table 54).

As we see from Table 54, only three large corporations - National Lead, Dupont de Nemours, and British Titan Products - account for about 60% of the capacity of the capitalist countries to produce this material.

Until very recently, the industrial production of titanium dioxide was based on the sulfuric-acid process for refining ilmenite concentrates, which will be discussed below. However, this method has very serious technological shortcomings and is inapplicable to many types of raw materials, e.g., concentrates with higher contents of chromium and other coloring impurities, leucosene- and rutile-containing concentrates, which dress poorly, and certain other forms of raw material. Technological flow charts that are free of these deficiencies are therefore urgently needed. This requirement is met by a method based on dressing of titanium-containing concentrates by the chloride method, with conversion of the resulting titanium tetrachloride into the dioxide. We shall show below that among the possible variants of titanium-dioxide production, the greatest advantages accrue to the reaction of titanium tetrachloride with oxygen in the so-called "combustion" of  $TiCl_4$ , which permits the design of a highly productive closed-cycle continuous titanium dioxide production process with return of the chlorine that is evolved into the cycle for chlorination of the titanium-containing starting material.

The method in which titanium dioxide is produced from  $TiCl_4$  has recently attracted serious attention in various countries, and in the USA in particular.

Dupont, which has spent, according to reports that have appeared in the periodical literature, 15 million dollars on development of a technology for this process [14], has set up the production of titanium dioxide by this method at several plants. This company's plant at New Johnsonville, Tennessee, which manufactures titanium dioxide from  $TiCl_4$ , has a production capacity of about 60 thousand tons per year. At the Edgemoor, Delaware plant, which has an annual capacity of 85 thousand tons of titanium dioxide, some of the product is also made from  $TiCl_4$ . A new plant was recently constructed at Antioch, California for production of titanium dioxide by the same method [43].

At the end of 1964, the Cabot Corporation began chloride-method operations at a plant at Ashtabula, Ohio, which has a capacity of 18 thousand tons of titanium dioxide per year [43]. Cabot purchased a license from the French firm de Thann et de Mulhouse for production of titanium dioxide by this method in the USA, Canada, and Mexico.

American Potash, which originally planned the construction of a plant for the production of titanium dioxide by an improved sulfuric-acid method [15], subsequently decided to convert to the chloride method, which yields  $TiO_2$  of higher quality [2, 16].

According to recently published data [43], this firm has a plant with a capacity of 22.7 thousand tons of  $TiO_2$  per year in the shakedown phase. American Cyanamid had plans to complete construction in 1965 on a plant with the same capacity at Savannah, Georgia. Two more firms - National Lead and Pittsburgh Plate Glass are adapting a chloride method for production of titanium dioxide at their own pilot plants. National Lead plans to construct a plant with a capacity of 18 thousand tons of titanium dioxide per year at Sayreville, New Jersey [43]. Thus, literature data indicate that recent American expansion of capacity and erection of new titanium-dioxide plants have been oriented practically exclusively to the chloride method, whose economy indicators are on a par with those of the sulfuric-acid method and which yields a higher-grade product. Published reports [68] indicate that the capital outlay required to build

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chloride-method plants is 20% lower than that required for sulfuric-acid installations.

Outside the USA, the chloride method has also attracted attention in other foreign countries - France, Great Britain, West Germany, and others, which are engaged in pilot-plant testing and organization of industrial titanium dioxide production on the basis of this method.

Thus, as we noted above, the French firm de Thann et de Mulhouse, which developed a technology for production of titanium dioxide from  $TiCl_4$  at its Thann plant [17], sold a license to the American firm Cabot for the production of titanium dioxide by this method. Plans call for use of the chloride method to produce about half (20 thousand tons) of the 45 thousand tons of new titanium dioxide production capacity to be developed in France over the next few years [6].

In Great Britain, a patent for the production of the dioxide from titanium tetrachloride has been taken out by the firm Laporte Industries, which, to judge from certain reports [2, 16], has joined forces with American Potash in the construction of a chloride-process plant at Mojave, California.

The problem of producing titanium dioxide from  $TiCl_4$  is closely related to that of producing metallic titanium, since the principal technological steps, including the acquisition of titanium-rich concentrates or slag smelting and the production and purification of titanium tetrachloride, are the same in the production of both metallic titanium and its dioxide. Where necessary, this makes it possible to combine production of the metal and titanium dioxide at the same plant.

This structuring of the plant may afford certain advantages. Having two products instead of one permits a sharp increase in the scale on which the titanium-containing raw material is converted to  $TiCl_4$ , from which either product can be made, with the consequent lowering of the net cost of the titanium tetrachloride and both of the final products. It also gives the plants flexibility for response to variations in demand, in that the

percentage of the titanium tetrachloride used to make either of these final products can be regulated, increasing the output of one of them at the expense of the other.

**Certain Properties and Applications**

Pure titanium dioxide is a white powder; on heating, it acquires a lemon-yellow color, which disappears again when it cools. Titanium dioxide is chemically inert and practically immune to attack by reagents - dilute mineral acids, hydrogen sulfide, sulfur trioxide, organic acids. Its solubility in alkalis is negligible. Below we list the solubilities of titanium dioxide in aqueous solutions of alkalis [20], in mg/100 ml of solvent:

|   |           |
|---|-----------|
| NaOH:   |           |
| 10% . . . . .   | 20-25     |
| 36% . . . . .   | 60-100    |
| KOH:  |           |
| 10% . . . . .   | 300-450   |
| 40% . . . . .   | 700-900   |
| KHCO <sub>3</sub> , saturated . . . . .               | 7000      |
| Na <sub>2</sub> CO <sub>3</sub> , saturated . . . . . | insoluble |
| K <sub>2</sub> CO <sub>3</sub> :                      |           |
| saturated . . . . .                                   | 300       |
| 30% . . . . .   | 20        |
| NaHCO <sub>3</sub> , 10% . . . . .                    | 250       |

Appreciable amounts of titanium dioxide dissolve in fused borax and phosphates [21]. It can be dissolved by prolonged heating with concentrated sulfuric acid (the solubility of TiO<sub>2</sub> decreases with rising calcining temperature), by reaction with hydrofluoric acid, or by melting it with potassium bisulfate. TiO<sub>2</sub> is a polymorphous oxide that is encountered in nature in three mineralogical forms with distinctive crystalline habits: rutile, anatase, and brookite. Of these three modifications of TiO<sub>2</sub>, brookite is unstable and practically never used.

The characteristics of rutile and anatase are given in Tables 29 and 55.

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TABLE 55

Characteristics of Rutile and Anatase Modifications  
of Titanium Dioxide [18, 19]

## Characteristics

## RUTILE

|   |  |
|---|--|
| Structure, lattice constants, Å         | Tetragonal; a = 4.58, c = 2.95   |
| Entropy, cal/(mole·deg)                 | 12.0 ± 0.05  |
| Enthalpy, cal/mole                      | $(400-1800^\circ \text{K}) H_T - H_{T90}^\circ =$<br>$= 17.97 T + 0.12 \cdot 10^{-3} T^2 + 4.33 \times$<br>$\times 10^5 T^{-1} - 6829$ |
| Molecular heat capacity, cal/(mole·deg) | $(298-1800^\circ \text{K}) C_p = 17.21 + 1.06 \times$<br>$\times 10^{-3} T - 3.59 \cdot 10^5 T^{-2}$                                   |

## ANATASE

|   |  |
|---|--|
| Structure, lattice constants, Å         | Tetragonal; a = 3.78, c = 9.49   |
| Entropy, cal/(mole·deg)                 | 11.93 ± 0.01   |
| Enthalpy, cal/mole                      | $(400-1300^\circ \text{K}) H_T - H_{T90}^\circ =$<br>$= 17.83 T + 0.25 \cdot 10^{-3} T^2 + 4.23 \times$<br>$\times 10^5 T^{-1} - 6757$ |
| Molecular heat capacity, cal/(mole·deg) | $(298-1300^\circ \text{K}) C_p = 17.14 + 0.98 \times$<br>$\times 10^{-3} T - 3.50 \cdot 10^5 T^{-2}$                                   |

A product of anatase or rutile structure is usually produced in the manufacture of titanium dioxide. As we see from Table 55, both of these modifications have the same crystallographic structure, but different lattice parameters; the latter are responsible for their property differences.

Roasting to metatitanic acid, the basic intermediate product in the production of titanium dioxide, which is produced by hydrolyzing titanium solutions, first produces anatase, which is converted to rutile as the temperature is raised further.

The structural change undergone by titanium dioxide on heating is of exceptional importance for its practical use. The temperature range and rate of the transformation depend on the method used to make the product and its impurity content. Thus, metatitanic acid produced by hydrolysis of titanium chlorides and nitrates, i.e., compounds with a univalent anion ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ), is

converted to rutile much more easily than acid produced by hydrolysis of sulfates, i.e., compounds with the divalent  $\text{SO}_4^{2-}$  anion. While metatitanic acid obtained by hydrolysis of aqueous titanium chloride solutions is converted to rutile quite rapidly even at around  $500^\circ\text{C}$ , a temperature about 300 degrees higher is required for the same intermediate product when it is produced by hydrolysis of sulfate solutions [22]. The rutile-transition temperature of metatitanic acid prepared by hydrolysis of titanium sulfate solutions depends on the conditions under which the acid formed. Thus, metatitanic acid obtained from dilute solutions is transformed to rutile on roasting at  $850^\circ\text{C}$ , while acid obtained from concentrated solutions undergoes the transformation only at  $950^\circ\text{C}$  [22]. For pure metatitanic acid with no impurities, the anatase-rutile transition temperature lies in the  $610\text{--}730^\circ\text{C}$  range, and the conversion is very rapid at the upper limit [23]; on the other hand, as we noted above, metatitanic acid prepared by sulfate hydrolysis undergoes the transition only in the  $850\text{--}950^\circ\text{C}$  range, apparently because of the presence of basic sulfates or sulfate ions that have been trapped by adsorption.

When certain impurities are present, the anatase-rutile transition may not take place even at higher temperatures. For example, not only  $\text{SO}_3$ , but also the presence of a small amount of impurity  $\text{SiO}_2$  in anatase inhibits its transformation to rutile, as does the presence of  $\text{HCl}$  in the surrounding atmosphere [24]. However, it would be advantageous to lower the temperature range of the anatase-rutile transition in view of the detrimental influence of high roasting temperature on the pigment properties of the titanium dioxide. This can be done by using titanium dioxide with additives of alkali vanadates,  $\text{K}_2\text{Cr}_2\text{O}_7$ , oxides of aluminum, magnesium, zinc, bismuth, antimony, calcium, or barium, or even water vapor and deposits having the structure of rutile [22, 25]. Some of these additives, such as aluminum oxide, not only promote rutilization, but also substantially increase the weathering ability of the pigment; this makes it advantageous to introduce about 1% of  $\text{Al}_2\text{O}_3$  on the weight of the  $\text{TiO}_2$  as an additive [26]. The physicochemical properties of rutile are also strongly affected by modifying its surface with certain compounds.

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For example, it has been shown that application of aluminum and silicon compounds to the surface of rutile improves its intensity, lowers its photochemical activity, and improves its resistance to sunlight and weather.

The structural changes of titanium dioxide during heating were studied in [27] by electron diffraction, differential thermal analysis, x-ray structural analysis, and electron microscopy.

It was established in this investigation that the activation energy of the anatase-rutile transition depends on the size of the anatase particles: the smaller the particles, the smaller the activation energy necessary to convert anatase to rutile.

The kinetics of the anatase-rutile transformation were recently studied in detail by Japanese investigators [28], who measured dielectric constants for the purpose (in consideration of the fact that anatase and rutile differ substantially in this property). The studies were made on specimens of pure titanium dioxide and specimens containing lithium and potassium chloride additives; they were heated at various temperatures in various environments.

The authors report that the conversion of anatase to rutile begins in the 750-800°C range in pure titanium dioxide specimens. The kinetic indicators of the process correspond to a first-order equation. As determined by the authors, the activation energy of the conversion for pure titanium dioxide in air is 110-116 kcal/mole. The rate of conversion of the anatase to the rutile modification is higher in an atmosphere of oxygen than in air; under these conditions, the process activation energy is 92 kcal/mole. When 1% of lithium chloride is introduced into titanium dioxide, the activation energy of the conversion is 150 kcal/mole.

Other studies have also been devoted to grain growth and phase transformations during calcination of titanium dioxide. In [29], for example, the influence of calcining temperature and small amounts of various oxide additives on the phase transformations was determined for titanium dioxide prepared by

decomposing titanium-ammonium sulfate, titanium oxalate, and titanium hydroxide.

When titanium dioxide is heated in an oxidizing atmosphere to moderately high temperatures (to approximately 600°C), it acquires a yellowish-brown color, which vanishes on cooling. However, calcining at excessively high temperatures (above 950°C) should be avoided, since partial thermal dissociation of the TiO<sub>2</sub> and the appearance of the colored lower oxides of titanium may cause an irreversible change in the color of the rutile - yellowing or darkening [22, 25]. Use of excessive temperatures in calcining rutile should also be avoided because of the danger of sintering and recrystallization of the dioxide particles, the result of which is a pigment of inferior quality [30].

TABLE 56  
Comparison of the Basic Physicotechnical Properties  
of Titanium Dioxide and Other White Pigments

| Pigment                                | Density,<br>g/cm <sup>3</sup> | Refractive<br>Index | Mohs<br>hardness | Particle<br>diameter μm | Relative<br>whiteness % | Covering<br>power m <sup>2</sup> /kg<br>paint |
|--|-------------------------------|---------------------|------------------|-------------------------|-------------------------|---|
| rutile . . . . .                       | 4.2                           | 2.76                | 6                | 0.3-0.25                | 98.9                    | 33  |
| anatase . . . . .                      | 3.9                           | 2.55                | 5.5              | 0.3-0.25                | 98.5                    | 33  |
| zinc whitening . . . . .               | —                             | 1.92                | —                | 0.12-5.0                | 99.7                    | 4.1   |
| lithopone . . . . .                    | —                             | 1.84                | —                | —                       | 97.8                    | 5.8   |
| lead whitening<br>(basic<br>carbonate) | 6.7-6.8                       | 1.94-2.09           | —                | 0.9-2.3                 | —                       | 3.1   |

Note. Covering power for painting over black strip.

Titanium dioxide is used in a number of industrial branches. However, one of the principal users of commercial titanium dioxide is the paint industry, which absorbs no less than half of the total amount produced.

As Table 56 indicates, the extensive use of titanium dioxide in the paint industry results from the superiority of the basic physicochemical properties of rutile and anatase over those of other white pigments [25], its lack of toxic effects, its chemical inertia, and its high resistance to atmospheric, chemical,

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We see from the data given in Table 56 that the covering power of titanium dioxide is several times greater than those of other white pigments; this makes it possible to economize greatly on materials and labor. The high covering power is a result of the high refraction coefficient and optimum particle size of titanium dioxide.

The color of titanium dioxide is strongly influenced by various impurities, and this must be taken into account in its production. Certain impurities are effective even at very small contents; this is not only because of mechanical mixing, but also because of the crystal-lattice distortion that they cause. Table 57 presents data on the influence of impurities on the color of titanium dioxide [22].

TABLE 57  
Influence of Impurities on the Color of Titanium Dioxide

| Oxide                          | Color imparted          | Smallest amount of impurity to produce visually discernible color, g/l of TiO <sub>2</sub> |
|--------------------------------|-------------------------|--|
| Cr <sub>2</sub> O <sub>3</sub> | brownish-yellow . . . . | 1.5 · 10 <sup>-4</sup>   |
| CdO                            | greyish yellow . . . .  | 7 · 10 <sup>-4</sup>   |
| CuO                            | greyish yellow . . . .  | 3 · 10 <sup>-4</sup>   |
| Fe <sub>2</sub> O <sub>3</sub> | yellowish grey . . . .  | 3 · 10 <sup>-4</sup>   |
| MnO                            | grey . . . . .          | 3 · 10 <sup>-4</sup>   |
| V <sub>2</sub> O <sub>5</sub>  | greyish-blue . . . . .  | 7 · 10 <sup>-4</sup>   |
| PbO                            | grey . . . . .          | 1 · 10 <sup>-4</sup>   |

As we see from Table 57, the whiteness of titanium dioxide is lowered most sharply by the chromium impurity. Anatase and rutile have different sensitivities to contamination by coloring impurities. Thus, while anatase remains white at a 0.009% Fe<sub>2</sub>O<sub>3</sub> content, rutile becomes yellowish even at a 0.003% content of this impurity [31]. This is explained by the different responses of the crystal lattices of the two titanium dioxide modifications to oxides of impurity elements, which are isomorphous with rutile in most cases and are incorporated into its crystal lattice. Thus, for example, an Fe<sub>2</sub>O<sub>3</sub> impurity gives rutile the yellowish

TABLE 58  
 Technical Specifications for Physicochemical Properties of  
 Pigment Titanium Dioxide in Anatase and Rutile Forms

| Property   | Standard for types |         |       |             |       |       |
|--|--------------------|---------|-------|-------------|-------|-------|
|  | A-1                | AV      | A-01  | R-1         | R-01  | R-02  |
| Whiteness, arbitrary units, no less than (in range)                    | 96.0               | 96-97   | 96.0  | 94.0        | 94.0  | 94.0  |
| Titanium dioxide content, %, not below                                 | 96                 | 96      | 94.5  | 96.5        | 96    | 93    |
| Rutile-form content, %, not below                                      | Not defined        |         |       | 96          | 95    | 95    |
| Moisture content, %, not below   | 0.5                | 0.5     | 0.5   | 0.3         | 0.3   | 0.3   |
| Water-soluble salt content, %, not above                               | 0.5                | 0.5     | 0.3   | 0.5         | 0.3   | 0.3   |
| pH of water extract  | 6.5-8              | 6.5-7.5 | 6.5-8 | 6.5-8       | 6.5-8 | 6.5-8 |
| Oil number, g of oil to 100 g of pigment, not above                    | Not defined        |         | 30    | 26          | 26    | 26    |
| Whitening power, arbitrary units, not below                            | 30                 | " "     | 1300  | 1500        | 1650  | 1650  |
| Covering power, converted to dry pigment, g/m <sup>2</sup> , not above | 1150               | " "     | 40    | 40          | 40    | 40    |
| Residue after wet screening on No. 0045K screen, %, not above          | 46                 | 0.1     | 0.05  | 0.2         | 0.05  | 0.05  |
| Content of particles smaller than 1 μm, %, not below                   | 0.2                | 94      |       | Not defined |       |       |

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coloration characteristic for an isomorphous mixture, while it turns anatase the characteristic light pink associated with ferric oxide [22]. The sensitivity of rutile to contamination by oxides of iron and other coloring elements (chromium, copper, vanadium, manganese, and others) also results in part from its distinct (by comparison with anatase) phototropism - its ability to turn dark and yellow in sunlight and recover its original whiteness in the dark [32, 33]. Phototropism is observed only in titanium dioxide specimens that are contaminated with oxides of coloring elements, and does not occur in pure  $TiO_2$ . According to literature data [32], this effect is due to a reversible process in which some of the oxygen is released from the  $TiO_2$  (under exposure to sunlight) and converts the impurity elements to higher oxides.

Titanium dioxide is currently being produced in both modifications - anatase and rutile. In conformity to the approved standard (GOST 9808-65), the Soviet industry is producing the following grades of pigment dioxide: A-1, AV, and A-01 in the anatase form and R-1, R-01, and R-02 in the rutile form.

The first two types of anatase titanium dioxide are untreated, while the third type is subjected to surface treatment with aluminum and silicon compounds.

Grade R-1 rutile titanium dioxide is untreated, R-01 is treated with aluminum and silicon compounds, and R-02 is treated with compounds of aluminum, silicon, and zinc.

The principal physicochemical properties of these grades must conform to the specifications and norms given in Table 58.

A comparison of the properties of rutile and anatase indicates the superiority of rutile, which has been responsible for its preferential use by the pigment industry. The most important advantage of rutile over anatase is its lower photochemical activity. The current view [22] is that the chalking and fading of paints is due to their photochemical activity, which stimulates oxidation of the surface layer of the coat under exposure to light and moisture. For this reason, rutile whites are more color-fast

than anatase whites when the coatings are exposed to the atmosphere [25]. Rutile is quite comparable with all types of vehicles. The effects of rutile whittings on the paint film are much weaker than those of anatase whittings, and this reduces chalking (a process in which vehicle is released from the film under exposure to light, chiefly in the ultraviolet) and peeling of the coat.

Along with its superiority over anatase as regards resistance to weathering, rutile also has disadvantages, including a definite if slight yellowish tint in the coatings; this is due to its lesser ability to reflect light in the violet and blue parts of the spectrum [25]. This is because of the previously noted more compact arrangement of the atoms in the crystal lattice of rutile and its higher density and refractive index. This deficiency can be eliminated by addition of tinting colors.

It has been established that various types of surface treatment applied to titanium dioxide - using white or colorless oxides, silicates, silicones and other compounds, have selective effects on specific properties of the pigment [34]. For example, treatment with aluminum hydroxide and silicon improves the resistance of the coatings to light and weather, treatment with silicones waterproofs the coatings and improves their resistance to humidity, and so forth. The treated pigments are much easier to disperse in the vehicle and rub free of lumps. In view of the high hardness of rutile, this is of substantial importance in reducing wear and increasing productivity in paint-grinding machines.

Aside from the paint industry, which is, as we noted above, one of the principal users of titanium dioxide, it is also applied in a number of other branches where its use offers substantial advantages. Thus, titanium dioxide is used in the metallurgical industry to produce titanium-containing hard alloys. In the synthetic-fiber industry,  $TiO_2$  is used to matte-finish artificial silk. In the paper industry, titanium dioxide makes paper white and opaque, thus permitting the manufacture of thinner and lighter papers. In the glass industry,  $TiO_2$  is used to produce special

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(thermostable and ultraviolet-transparent) types of glass. The high dielectric constant of titanium dioxide (78 for anatase and up to 180 for rutile) makes possible its use for the manufacture of high-grade dielectrics for capacitors and radio apparatus [22].  $TiO_2$  is also used in electric welding to coat welding wires and in a number of other engineering branches.

It is reported that the paint industry of the USA, which is a major producer of titanium dioxide, used as much as 60% of the entire output in 1960 [1]. The approximate figures for the amounts of titanium dioxide used by other branches were as follows: paper industry 14%, rubber industry 5%, plastics industry 6%, leather industry 2%, textile industry 3.5%, electric welding (welding-wire coating) 1.5%, others 8%.

The following distribution of titanium dioxide use among the various fields of application was reported in West Germany for the same year [35]: paint industry more than 40%, plastics production 11%, paper industry 9%, porcelain 8%, textiles 7%, rubber 6.5%, leather, synthetic fibers, and other materials 6%, welding electrodes 3.5%, other fields of application about 9%.

According to recently published data [69], the paint industry remained the largest field of application for titanium dioxide in the USA in 1965, consuming 55% of the total amount used in that country. In that year, titanium dioxide use was distributed as follows among the other fields of application: paper 20.7%, floor coverings (linoleum, etc.) 4.7%, rubber 4.2%, plastics 2.6%, graphic arts 2.1%, remainder divided among other fields of application.

## Chapter 28

## BASIC METHODS OF TITANIUM DIOXIDE PRODUCTION

## The Sulfuric-Acid Method

A number of chemical methods have been proposed for processing titanium-containing raw materials into titanium dioxide. Without dwelling here on a description of these methods, which are set forth in a number of literature sources [20, 36, 37, 67, and others] and are not part of the subject matter of this book, we note only that the most widespread method of  $TiO_2$  production, and the one on which the industrial technology of this compound was based almost exclusively until quite recently both in the USSR and abroad is the sulfuric acid method. It can be used to refine ilmenite concentrates and the titanium slags obtained on reductive electric-arc melting of these concentrates.

For comparative evaluation of the method in which titanium dioxide is produced directly from  $TiCl_4$  with the sulfuric-acid method, let us briefly discuss the basic features of the latter method.

The sulfuric-acid method is a complex multistage process. However, the numerous technological operations (Fig. 143) can, in principle, be reduced to three basic stages: dressing of the raw material to produce titanium sulfate solutions and purification of these solutions; hydrolysis of the solutions to produce titanium hydrates; roasting of the hydrates to convert them to

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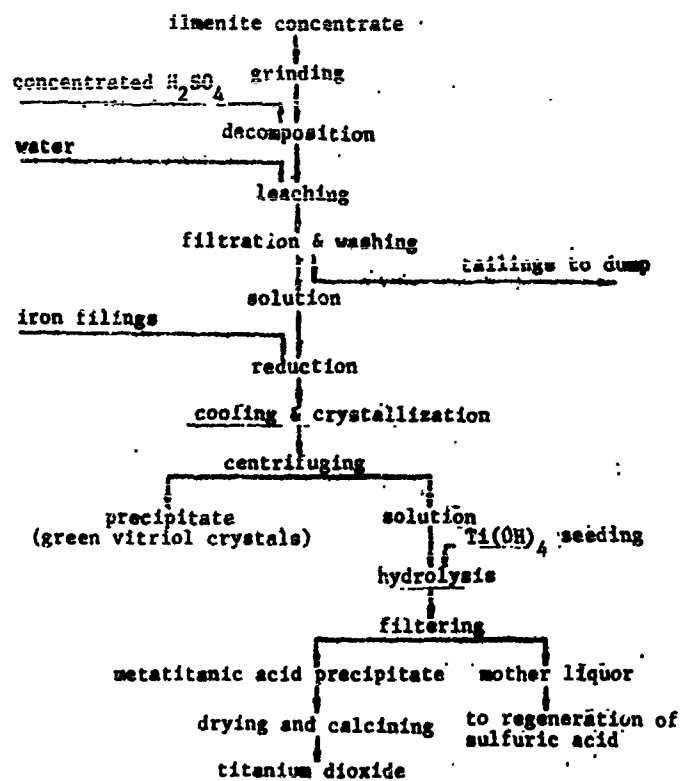
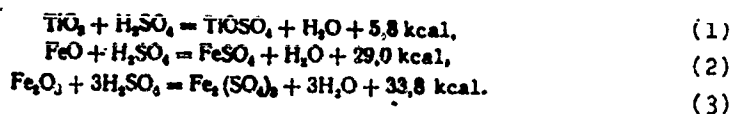


Figure 143. Flow chart of titanium dioxide production from ilmenite concentrate.

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For the first stage of the process - the production of titanium sulfate solutions - the titanium-containing raw material (ilmenite concentrates, slags) are ground fine and treated, with heating and vigorous agitation, with sulfuric acid; decomposition of the titanium and iron oxides results in formation of the sulfates of these elements in accordance with the following thermochemical equations:



The exothermic heat of all of these reactions and the heat liberated on addition of water to the concentrated sulfuric acid help the acid break the raw material down.

Depending on their acidity, which is characterized by the acid factor,<sup>(1)</sup> the titanium sulfate solutions may vary in stability. The so-called unstable solutions become turbid and form a sediment even on standing for a short time, while stable solutions can be stored for a long time without undergoing changes. Thus, for example, titanium sulfate solutions containing 120 g/liter of  $\text{TiO}_2$  are unstable at acid factors below 1.7-1.8 and stable when the factor exceeds 1.8-2.0 [22].

There are three known versions of the periodic process in which ilmenite is decomposed by sulfuric acid: liquid-phase, intermediate-phase, and solid-phase; they differ in the concentration of the sulfuric acid used and the nature of the decomposition products formed [36].

However, the solid-phase process is most commonly used in industrial practice, since it breaks the concentrates down most quickly and completely and produces solutions of higher basicity, thus promoting hydrolysis and making it easier to obtain a final product of higher quality.

Concentrated sulfuric acid is used in this ilmenite-decomposing process, so that the temperature of the reaction mixture

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Footnote (1) is on page 740.

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may be raised quickly to 190-220°C (it is possible to obtain a sharp temperature rise by adding water or hydrolysis acid to the concentrated acid); this gives a fast process and a high degree of concentrate decomposition, of the order of 96-97%. After leaching, the resulting titanium sulfate solutions have low acid factors (around 1.8). Without dwelling on the technology and equipment of this process, which are described in detail in the corresponding literature [22, 36, 39], we note that continuous ilmenite-decomposition processes have been proposed along with periodic ones.

One of these methods was developed in Canada by N. Solodukha (Continental Titanium Corporation). In the Solodukha process [40], ilmenite is decomposed with 40-45% sulfuric acid produced by mixing hydrolysis and fresh acids. The process is run at 254°C and an absolute pressure of 21 atm in a steam-heated tubular reactor. To prevent a crust from forming inside the reactor, the sulfuric-acid treatment is accompanied by vigorous pump circulation.

This method has advantages over the prevailing sulfuric-acid process. Since the acid can be dilute, acid formed in the titanium sulfate hydrolyzing operation can be used to break down the raw material. The continuity of the process lowers capital investment and labor costs. As is noted in the literature [41], this opens the way to lowering the cost of titanium dioxide by 25-30% as compared with the existing sulfuric-acid process.

The principle of another method [22, 39], which is illustrated schematically in Fig. 144, consists in decomposing the ilmenite in a twin-screw mixer, to which it flows through a pipe in the form of a controllable stream of fuming-acid suspension<sup>(2)</sup> that has been prepared in a water-cooled drum with a stirrer. Heat is liberated by diluting the fuming acid with water to a 90% H<sub>2</sub>SO<sub>4</sub> concentration, and this stimulates the decomposition reaction, thickening the suspension. The melt obtained as a result of decomposition solidifies in the worm, and is ground up and sent for leaching.

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Footnote (2) is on page 740.

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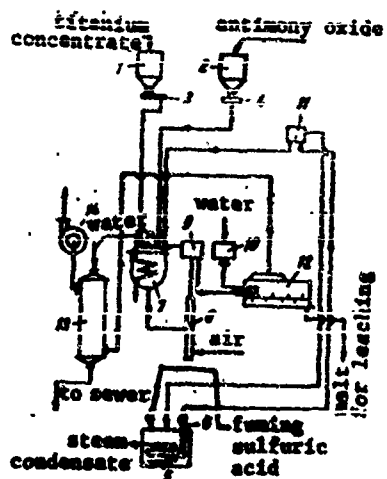


Figure 144. Diagram of continuous decomposition of ilmenite concentrate [22]. 1) Titanium concentrate hopper; 2) antimony oxide hopper; 3) batching worm; 4) antimony oxide batcher; 5) fuming sulfuric acid reservoir; 6) submerged pump; 7) mixer for fuming sulfuric acid and concentrate; 8) air lift; 9) batcher for mixture of fuming sulfuric acid and concentrate; 10) water batcher; 11) fuming sulfuric acid batcher; 12) equipment for continuous decomposition; 13) gas-trapping scrubber; 14) fan.

remains in the solution, but this is not enough to interfere with subsequent hydrolysis. The titanium sulfate solutions obtained after crystallization of the green vitriol, which contain the equivalent of about 140-150 g/liter of  $TiO_2$ , are concentrated and sent for hydrolysis.

To accelerate the operation and improve the quality (dispersion) of the resulting hydrates, hydrolysis is carried out by boiling in the presence of seed crystals from titanium sulfate

The titanium sulfate solutions obtained after leaching of the melt also contain ferrous and ferric sulfates. To prevent precipitation of trivalent iron salts into the deposit together with the metatitanic acid during hydrolysis, they are reduced to the divalent form, and much of the  $FeSO_4$  is, in turn, removed from the solution by crystallization. The trivalent iron present in the solution is reduced with iron filings or electrolytically until the solution is turned violet by the trivalent titanium ions that form (until it contains the equivalent of 2-3 g/liter of  $Ti_2O_3$ ); the violet can appear only when all of the iron has gone over to the divalent form. Then the  $FeSO_4$  is removed from the solution by using the sharp drop in its solubility with temperature. The solution is cooled, e.g., to  $-2^\circ C$  (with a cooling brine) to freeze out green vitriol  $FeSO_4 \cdot 7H_2O$ . At this temperature, 20-22 g/liter of ferrous oxide re-

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solutions containing no less than 190-200 g/liter of  $TiO_2$  and having acid factors greater than 2. Without dwelling here on the technological conditions of hydrolysis [22] or the highly complex mechanism of the process [42], we note only that this operation, whose net equation is  $TiOSO_4 + 2H_2O \rightarrow H_2TiO_3 + H_2SO_4$  results in formation of a large amount (the equivalent of about 2 tons of the monohydrate to one ton of  $TiO_2$ ) of dilute, 20-22% hydrolysis sulfuric acid contaminated by iron sulfate, 1-2% of titanil sulfate, and a few percent of other sulfates; this is a waste product for whose recycling most plants make no provision.

From the standpoint of utilizing the hydrolysis sulfuric acid, interest attaches to a proposal for sulfatizing the titanium-containing materials in a vertical fluidized-bed furnace, combining breakdown of the raw material with concentration of the hydrolysis acid by evaporation.<sup>(3)</sup> This would permit breaking the concentrates down in a continuous process and produce the sulfatization product in granular form, thus making its subsequent refinement easier.

One possible way to utilize the hydrolysis acid might be steaming down in a Nordak-type apparatus to 55% concentration with subsequent utilization of the product in superphosphate production.

Up to 95-96% of the Ti goes into the precipitate during hydrolysis, and the metatitanic acid that is formed sorbes a substantial amount of  $SO_3$ . The metatitanic acid is then washed, dried, and roasted, which results in elimination first of the water (at 200-300°C) and then of the  $SO_3$  (at 500-800°C), with formation of the neutral (pH = 7) product, titanium dioxide, at about 850-900°C.

The byproduct of the process - ferrous sulfate heptahydrate - is roasted to produce the monohydrate  $FeSO_4 \cdot H_2O$  and ground.

The approximate amounts of the base materials used in the production of one ton of titanium dioxide from ilmenite concentrates by the sulfuric-acid process are as follows [22], in tons:

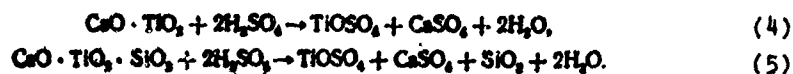
Footnote (3) is on page 740.

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| Ilmenite concentrate (containing 42% TiO <sub>2</sub> ) . . . . . | 3.1     |
| Sulfuric acid (monohydrate) . . . . .                             | 4.0-4.5 |
| Iron filings . . . . .  | 0.24    |

As we noted above, titanium slags produced by ore-reduction smelting of ilmenite concentrates may also serve as a source for TiO<sub>2</sub> production. Slags are used, for example, at the rather large Canadian plant (20,000 tons of titanium dioxide per year) recently placed in operation near Sorel in Quebec [45].

Data available in the literature permit a comparative technical evaluation of the processes in which the dioxide is produced from titanium slags and ilmenite concentrates [44]. When titanium dioxide is produced from slags by the sulfuric-acid method, the solutions obtained after leaching out the titanium sulfate, which contain about 190 g/liter of TiO<sub>2</sub> with low iron contents, are more easily hydrolyzed than in the case of ilmenite-concentrate processing. The resulting hydrolysis acid contains only about 9 g/liter of Fe, which makes it easier to regenerate. Moreover, in addition to the high-titanium slags (80-85% TiO<sub>2</sub>), it has been found possible to convert 42-55% (TiO<sub>2</sub> equivalent) slags into titanium dioxide. This opens the way to the use of slags obtained by electrosmelting of titanomagnetites - a highly important prospect, since the USSR has large reserves of ores of this type, complex processing of which should permit extraction of iron, titanium, and other valuable components from them simultaneously.

In addition to ilmenite, the USSR also has a number of other forms of titanium-containing ores, chiefly composite types, that might become important sources for titanium dioxide production. These sources include primarily perovskite and sphene, the reserves of which are very large. However, the conditions of dressing of perovskite and sphene concentrates with sulfuric acid differ substantially from those for ilmenite or slags, since the process generates a large amount of sludge in the form of calcium sulfate or a mixture of this sulfate with silica:



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Sphene is broken down comparatively easily with sulfuric acid [46]. On boiling for 12-16 hours in 50% H<sub>2</sub>SO<sub>4</sub>, up to 90% of the TiO<sub>2</sub> goes into solution, and as much as 95% is dissolved in concentrated sulfuric acid. Perovskite is much harder to break down, and its decomposition requires excesses of sulfuric acid; however, this raises the acidity of the titanium sulfate solutions, with the result that they become unsuitable for the production of pigment (finely dispersed) grades of titanium dioxide [22]. I.V. Riskin et al. established conditions that make it possible to increase the degree of decomposition of perovskite with solutions of normal acidity, but conduct of the process is greatly complicated by sludge, which is formed in large quantities - approximately 2.5-3 tons per ton of TiO<sub>2</sub> [22].

Processing of these raw-material types can be made economically feasible only with a technology that provides for complex utilization of all valuable components. The literature describes a number of basic process flow charts that have been proposed for processing these types of titanium-containing raw materials [44, 47-52]. Without dwelling here on these processes, we note only that few of them have been elaborated to the industrial-testing and adaptation stages. And, until recently, other forms of ore material, such as rutile- and leucoxene-containing concentrates, while of substantial practical interest, have not yet been put to use because of the difficulty of preparing them for sulfuric-acid processing.

Among the ore raw materials, therefore, the ilmenite concentrates are now most suitable for processing by the sulfuric-acid method. At the same time, it follows from the above that the existing industrial process in which titanium dioxide is obtained from ilmenite by sulfuric-acid treatment has a number of important drawbacks, principal among which are the complex multistage flow of the process and the large amount of sulfuric acid consumed, much of which goes unproductively into the formation of large amounts of wastes - iron sulfate (more than 3 tons of the heptahydrate for each ton of TiO<sub>2</sub>) and dilute (20-22%) and contaminated hydrolysis sulfuric acid.

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It is also necessary to note that the development of large-scale industrial titanium dioxide production by the sulfuric acid process requires major capital investments in additional sulfuric-acid production capacity.

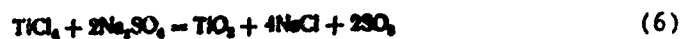
Thus, along with improvement of the existing sulfuric-acid process for titanium dioxide production from ilmenite concentrates or titanium slags, serious attention must be given to new and advanced technologies, most important among which are method for direct production of this compound from titanium tetrachloride.

#### Production of the Dioxide from Titanium Tetrachloride

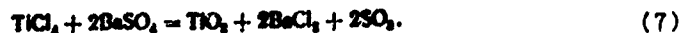
The following basic processes are possibilities for production of titanium dioxide from  $TiCl_4$ :

1. Hydrolysis of titanium tetrachloride in aqueous solutions.
2. Hydrolysis of titanium tetrachloride in steam (vapor-phase process).
3. Reaction of titanium tetrachloride with oxygen or an oxygen-containing gas (the "combustion" process).

Methods other than the above have also been proposed. For example, one of them suggests that the use of water, steam, or oxygen-containing gas be eliminated and that the titanium dioxide be obtained by reacting titanium tetrachloride with sulfates by the reactions



or



However, neither the degree of titanium tetrachloride utilization nor the quality of the titanium dioxide product obtained in these processes has been satisfactory.

#### Production of Titanium Dioxide by Hydrolysis of Titanium Tetrachloride in Aqueous Solutions

The chemical mechanism of titanium tetrachloride hydrolysis in aqueous solutions makes it a highly complex process, in which, depending on conditions and the completeness of the reactions, titanium oxychlorides and hydroxychlorides of variable

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composition may be formed [42, 53-56]. To produce titanium dioxide by this method, it is first necessary to prepare aqueous solutions of the titanium chloride, which are then subjected to hydrolysis. In preparing these solutions, it must be remembered that on dissolving in water, titanium tetrachloride is converted quickly to chloroxides and hydroxides with more or less water of hydration, and that these compounds make the solution initially turbid. However, then can be redissolved by introducing additional amounts of anhydrous titanium tetrachloride into the solution [42].

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Research has shown that precipitation is promoted by a substantial temperature increase during hydration. Thus, if no cooling is provided during solution of the  $TiCl_4$ , the solution temperature rises above  $100^{\circ}C$  until the titanium concentration has reached the equivalent of 130 g/liter of the dioxide and the equivalent of 250 g/liter of hydrochloric acid.

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As dissolution continues, solution temperature decreases owing to the evolution of hydrogen chloride, whose heat of vaporization exceeds the heat of solution of anhydrous titanium tetrachloride. Partial elimination of the hydrogen chloride also explains why the molar ratio  $Ti:Cl$  in the solution usually differs from theory.

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The literature [42] notes that better results are obtained in preparation of the aqueous titanium chloride solutions if dilute hydrochloric acid is used as the primary solvent instead of water. In this case, the hydrogen chloride begins to evolve at a lower temperature as the titanium tetrachloride dissolves, with the result that overheating of the solution is not as severe and smaller amounts of hydrated deposits settle out. To eliminate local hot spots during preparation of the titanium chloride solution, it is necessary to agitate vigorously. The concentration of the resulting clear titanium chloride solutions is the equivalent of about 350 g of  $TiO_2$  per liter.

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The principal production operation in this process - hydrolysis of the aqueous titanium chloride solutions - proceeds in several stages, as in the case of titanium sulfates, and is

chemically quite complex. Polytitanium hydrates and oxides with various space lattices, which sometimes contain chlorine residues in the molecule, form during hydrolysis. This hypothesis is confirmed, for example, by the fact that when  $TiCl_4$  dissolves in water, the viscosity of the solutions rises sharply in a manner not consistent with the actual solubility [42].

Hydrolysis can be carried out in two ways - in the presence of seed crystals or by dilution of the concentrated solutions.

In the former method, seed crystals are started in a small portion of the titanium chloride solution after lowering its acidity to  $pH = 2-3$  by neutralization or dilution, and then the rest of the solution is added; hydrolysis proceeds quite rapidly on heating. In the latter method (without use of the seed crystals), hydrolysis is initiated by introducing the concentrated titanium chloride solution into hot water, followed by boiling.

In the final analysis, hydrolysis results in formation of metatitanic acid, which is then roasted to obtain titanium dioxide.

Titanium dioxide produced by hydrolysis of titanium tetrachloride from aqueous solutions is of high purity if a purified starting material is used. Production of pigment dioxide by this process requires less purity of the  $TiCl_4$  than other methods (paraphase\* or combustion in oxygen-containing gas), since most of the harmful impurities remain in the hydrolysis hydrochloric acid solutions. However, it must be remembered that liquid-phase hydrolysis of titanium tetrachloride is greatly complicated by partial suspension of the precipitated hydrate; it is quite difficult to wash the chlorine out of this suspension and filter it. Moreover, the titanium dioxide produced by this method has comparatively poor pigment properties. It has been reported [22] that the pigment properties of the product can be improved by hydrolyzing titanium chloride solutions to which sulfuric acid or sodium sulfate has been added (in amounts representing 20-30% of the  $TiO_2$ ) and by roasting the product with potassium or sodium carbonate.

\*Translators Note: This may also possibly mean vapor phase.

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In addition to the above, it must be borne in mind in evaluating aqueous-solution hydrolytic decomposition of titanium tetrachloride that it involves waste in the form of dilute hydrolysis hydrochloric acid.

Hydrolysis of titanium tetrachloride in aqueous solutions has not come into practical use; it may be found useful only for preparation of titanium dioxide of high purity on a small scale.

Production of the Dioxide by Hydrolysis of Titanium Tetrachloride in Steam (Vapor-Phase Method)

Like that of aqueous-solution hydrolysis, the chemical mechanism of titanium tetrachloride hydrolysis in the vapor phase is quite complex. According to literature data, hydrolytic decomposition of  $TiCl_4$  begins immediately when its vapor is brought into contact with steam; oxy- and hydroxychlorides of tetravalent titanium form first and are subsequently converted to titanium dioxide as the temperature rises [57, 58]. L.N. Shchegrov and Ya.Ye Vil'nyanskiy [59, 60] showed that in the 125-450°C temperature range, vapor-phase hydrolysis of  $TiCl_4$  results in formation of titanium oxychlorides and hydroxychlorides and also the dioxide, the content of which in the products increases with rising hydrolysis temperature. Complete hydrolytic decomposition of titanium tetrachloride occurs at temperatures above 500°C. Under these conditions, however, the titanium dioxide initially formed by the reaction between the titanium tetrachloride and the steam is in the anatase rather than the rutile form; this form is gradually converted to rutile only on holding in the reaction space at temperatures of 900°C or higher.

In addition to temperature and the steam excess, the degree to which the titanium tetrachloride vapor is diluted with neutral gas, such as nitrogen, is a factor with a strong influence on the grain size of titanium dioxide produced by the vapor-phase method. To produce pigment titanium dioxide of the required granulometric composition (with a majority of the grains in the approximate size range from 0.2 to 0.3  $\mu m$ ), it is recommended that rather high dilutions (e.g., 5-6-fold) be employed. However, the literature indicates that it is not possible even then to prevent the

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formation of a certain amount of coarse-grained product (up to 10%) that is unsuitable for use as a pigment; this material is a waste product of the process.

The patent literature indicates the possibility of using various technologies to produce pigment titanium dioxide by vapor-phase hydrolysis of  $TiCl_4$ . These processes can be reduced to the following three basic variants on the basis of their temperature conditions:

a) a low-temperature process, in which the  $TiCl_4$  is hydrolyzed and the reaction products are subsequently held at comparatively low temperatures (of the order of 300-400°C);

b) a combined, or two-stage, process in which the  $TiCl_4$  is hydrolyzed at a temperature below the holding temperature of the product, e.g., 400°C (the holding temperature is at least 900-1000°C);

c) a high-temperature process in which the  $TiCl_4$  is hydrolyzed and the products are held at the same comparatively high temperature (not below 900°C).

A number of patents have been issued for processes in which titanium tetrachloride is vapor-phase hydrolyzed at low temperatures.<sup>(4)</sup> We present the following process flow to illustrate the low-temperature hydrolysis.

Two streams of air bubbled through separate liquid containers become saturated with vapor: one with titanium tetrachloride (at 120°C) and the other with water vapor (at 80°C). The volume proportions of  $TiCl_4$  and  $H_2O$  in the vapor-air mixture are about 1:1. The two vapor-gas mixtures are heated separately to the process temperature (400°C) before they are fed into the reaction space in order to prevent undesirable reactions; they flow simultaneously into a vertical cylindrical vessel -- the hydrolyzer, which has been heated externally to the same temperature. One liter of the mixture of air with water vapor (0.5 liters of  $H_2O$  vapor) and 0.1 liter of the mixture of air with titanium

Footnote (4) is on page 740.

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tetrachloride vapor (0.05 liter of  $TiCl_4$  vapor) are supplied per cubic decimeter of reaction space per minute. The two streams mix in the reaction zone, form titanium dioxide and hydrogen chloride, and descend into a dust chamber, which has been heated to a temperature from 200 to 400°C in order to prevent condensation or adsorption of HCl on the precipitated  $TiO_2$  particles. The hydrogen chloride is recovered after it leaves the dust chamber.

The originators of the low-temperature vapor-hydrolysis report that the resulting titanium dioxide contains practically none of the oxy- and hydroxychlorides, and that the yield is almost stoichiometric; the product does not require supplementary roasting, and its covering power equals that of pigment produced from sulfate solution and calcined at 900°C.

This claim stands in contradiction to the above remarks on the chemical mechanism of the hydrolytic decomposition of titanium tetrachloride and to statements made by the authors of the two-stage version, who report that the products obtained at 400°C without high-temperature calcining have the anatase structure and cannot be used directly as a pigment because they contain 2-3% HCl and undecomposed titanium oxychloride. It is reported that this disadvantage can be avoided by using the two-stage process, in which the product can be purified of both HCl and titanium oxychloride by high-temperature holding.

A number of practical variants have been proposed for the two-stage process. For example, the authors of certain patents<sup>(5)</sup> recommend that titanium dioxide be produced by reacting the tetrachloride with steam in the presence of inert solid water-soluble salts, such as alkali-metal chlorides or sulfates. Thus, for example, 100 parts (by mass) of titanium tetrachloride are mixed with 200 parts (by mass) of finely divided potassium sulfate to form a thick plastic mass. This mass is heated to a temperature from 300 to 400°C, at which a current of steam is passed over it for 1 hour. The temperature is then brought up to 800-900°C and

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Footnote (5) is on page 740.

held for 15 to 30 minutes, after which the mass is cooled to room temperature and leached out with water to remove the potassium sulfate. The titanium dioxide left in the residue is washed, dried, and ground.

The two-stage process for steam hydrolysis of titanium tetrachloride in the presence of inert water-soluble salts is more cumbersome and complex than the two-stage process in which these salts are not used. One recent American proposal<sup>(6)</sup> for such a two-stage process calls for running it sequentially in two reaction zones. In the first, low-temperature (343°C) zone, the titanium tetrachloride reacts with oxygen and hydrogen-containing gases, with titanium dioxide and hydrogen chloride as the hydrolysis products. In the second zone, whose temperature must be above 650°C, most of the titanium tetrachloride reacts with an oxygen-containing gas in the presence of the dioxide produced by hydrolytic decomposition of  $TiCl_4$  in the first zone.

Fully satisfactory results would appear to be unlikely in the two-stage variant, especially when inert water-soluble salts are used. The product obtained from the two-stage process is not completely free of HCl (containing 0.2-0.4% of this acid). Moreover, the titanium oxychloride formed during the low-temperature stage of the process gives a coarse-grained product when it decomposes during high-temperature holding; acquisition of high-grade titanium dioxide by the secondary reaction of the chloroxide with water vapor is also difficult. As a result, such titanium dioxide is unsuitable for use as a high-grade pigment.

The most satisfactory results are obtained in the high-temperature variant of steam hydrolysis of titanium tetrachloride, in which the process is run at temperatures in excess of 900°C. The literature indicates that hydrolysis proceeds rapidly under these conditions, yielding finely divided titanium dioxide in the rutile modification with satisfactory pigment properties.

To make it easier to supply the reaction equipment with the heat needed for high-temperature hydrolysis, it is recommended

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Footnote (6) is on page 740.

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that the titanium tetrachloride be reacted not with steam, but with an oxyhydrogen mixture:



It has been reported [61] that when a 2:1 hydrogen-to-air ratio is used, it is possible to obtain a high-grade product containing 99.72%  $\text{TiO}_2$  in particle sizes from 0.2 to 0.4  $\mu\text{m}$ .

Rather high process productivity must be ensured in the vapor-phase hydrolysis of titanium tetrachloride, since large hydrolyzers are required when the vapor-gas mixture moves slowly through the reaction space; this complicates heating of the hydrolyzers and requires more production floorspace.

Proposals have therefore been submitted with the object of increasing the productivity of the vapor-phase titanium-dioxide production process by improving the design of the production process. Special attention has been given to the provision of strong circulation of the vapor-gas mixture in the reaction chamber,<sup>(7)</sup> since this helps raise the rate of the titanium-tetrachloride hydrolysis.

There is no doubt that other ways will also be found to step up the vapor hydrolysis of titanium tetrachloride. Even then, however, we shall be left with a highly important disadvantage of the vapor-phase method: the impossibility of devising a closed production cycle for the chlorine in which it is returned directly into the process for chlorination of the starting titanium-containing raw material to produce titanium tetrachloride. From this standpoint, substantial interest attaches to the method described below for the production of titanium dioxide by "burning" titanium tetrachloride in an oxygen-containing gas.

Production of the Dioxide by Reacting Titanium Tetrachloride with an Oxygen-Containing Gas (the "Combustion" Method)

When oxygen or an oxygen-containing gas reacts with titanium tetrachloride, the products include gaseous chlorine as well as titanium dioxide. The chlorine can be recycled, either directly

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Footnote (7) is on page 740.

or after regeneration from the diluted gas mixture, for chlorination of the titanium-containing raw material. This is why the "combustion" of titanium tetrachloride has attracted so much attention. As we mentioned above, pilot plants and full-scale plants have recently been built in a number of developed industrial countries for production of titanium dioxide by this method.

However, despite the strong practical interest in producing titanium dioxide by reacting titanium tetrachloride with oxygen, no information on the problem appeared in the technical literature until quite recently, and patent applications were the only source of data on the process.

It has been established by tensimetric analysis [62] that the reaction of titanium tetrachloride with oxygen is described quite accurately by the equation



This conclusion is in full agreement with the data of L.N. Shchegrov [63], who showed that no titanium oxychlorides are formed in the reaction of titanium tetrachloride vapor with dried oxygen and that the products of this reaction are titanium dioxide and molecular chlorine.

It was established by thermodynamic analysis of the reaction in [62] that the temperature curve of the isobaric potential of the "combustion" of titanium tetrachloride corresponds in the case of titanium dioxide of the rutile structure to the equation

$$\Delta Z^0 = -48755 - 2,977 \lg T + 20,027 - 0,00 \cdot 10^{-3} T^2 \quad (10)$$

and in the case of the anatase dioxide to the equation

$$\Delta Z^0 = -37729 - 2,81 T \lg T - 0,55 \cdot 10^{-3} T^2 + 23,36 T \quad (11)$$

Below we give values of  $-\Delta Z^0$  for the two titanium dioxide modifications at various temperatures.

| temp., °C | rutile | anatase | temp., C° | rutile | anatase |
|-----------|--------|---------|-----------|--------|---------|
| 300       | 49106  | 38063   | 900       | 38010  | 21174   |
| 400       | 41219  | 27290   | 1000      | 36002  | 19000   |
| 500       | 32284  | 20329   | 1100      | 35198  | 18767   |
| 600       | 26378  | 24966   | 1200      | 34437  | 17986   |
| 700       | 20498  | 23881   | 1300      | 33689  | 16438   |
| 800       | 17640  | 23408   |           |        |         |

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It follows from these  $\Delta Z^0$  that formation of titanium dioxide with both the rutile and anatase structures is thermodynamically possible when titanium tetrachloride reacts with oxygen.

It was shown in [62] that no titanium dioxide is formed when these reactants interact at temperatures below 700°C. The reaction advances at an appreciable rate only beginning at temperatures of the order of 700°C, and its rate increases with rising temperature (especially sharply around 1000°C).

The structure and granularity of  $TiO_2$  obtained by burning titanium tetrachloride in oxygen has been studied with the aid of an automatic-recording x-ray unit and an electron microscope. It was established that when titanium tetrachloride is burned at temperatures below 1000°C, the product is the anatase form of titanium dioxide. The rutile content in the product increases as the process temperature is raised above 1000°C.

To ascertain the conditions for conversion of the anatase to the rutile form in titanium dioxide produced by burning titanium tetrachloride, anatase that had been formed at 700°C was heated for one hour at 1000 and 1100°C. It was found that a small amount of the anatase form still remained in the product in the former case. In the latter case (1100°C), all of the titanium dioxide assumes the rutile form, but the grains are coarsened considerably.

Since 1959, the Institute of Metallurgy of the USSR Academy of Sciences has also been studying the reaction of titanium tetrachloride with oxygen [64]. The studies were made in an externally preheated quartz laboratory reactor of small capacity. When the combustion process was run at 1150°C, the product was a mixture of the rutile (50-60%) and anatase (40-50%) modifications of titanium dioxide. It was established that the time spent by the titanium dioxide in the hot zone of the reactor is of decisive importance in determining grain size; it is recommended that this time be limited at all costs to 15-20 sec.

Although, as we noted above, titanium tetrachloride vapor can be converted quickly and completely into the dioxide by reacting it with oxygen or air at high temperature, major technical

difficulties are encountered in attempts to produce material that meets the requirements of the pigment industry.

The basic difficulties that must be overcome to ensure a normally functioning process include:

a) obstruction of the pipes by the solid product as it forms; this interferes with smooth delivery of the reactants into the unit and continuity in the titanium-dioxide production process;

b) deposition of titanium dioxide in the reaction chamber in substantial thicknesses and its stubborn adhesion to the walls of the apparatus. Such deposits upset the gas dynamics of the process and are detrimental to the quality of the product; they also cause major difficulties in supplying heat to the reaction zone (when the unit is externally heated);

c) the need to supply enough heat to the reaction zone to "oxidize" the titanium tetrachloride at a high rate;

d) the complex task of selecting structural materials for industrial apparatus that are chemically stable at the high temperatures and in the aggressive media (titanium tetrachloride, chlorine) that are used;

e) the need to eliminate or control recrystallization and grain growth of the titanium dioxide particles.

Below we examine a number of methods that have been proposed for production of titanium dioxide by combustion of  $TiCl_4$ .

Although the reaction between titanium tetrachloride and oxygen is exothermic, the heat released is not enough to keep the reaction going spontaneously. For normal combustion of the titanium tetrachloride, therefore, it is necessary to supply a certain amount of heat — depending on scale — to the reaction apparatus from the outside [65]. As the literature notes, this can be done in any of the following three ways (or a combination thereof): external heating of the apparatus; preheating of the reactants to the necessary temperature before they are introduced into the reaction space; introduction of a combustible gas or vapor into the vapor-gas mixture.

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A number of patents have been issued for each of these versions. Despite the fact that some of them differ considerably as regards the form of the process equipment, many of the patents for titanium-tetrachloride combustion propose reactors whose designs are essentially similar.

A schematic diagram of one of these reactors appears in Fig. 145. It consists of a vertically positioned cylindrical reaction chamber (tube) 2, which has a tapered bottom 4 for collection and unloading of the titanium dioxide that settles and an exit orifice 3 for the dust-gas mixture, from which the rest of the  $TiO_2$  is separated (on an electrostatic or sleeve filter). The burner (nozzle) 1, which may consist of two, three, or concentric tubes that form annular passages for introduction of the reagents into the chamber, is positioned at the top of the reactor (Fig. 145 shows a horizontal section through these tubes).

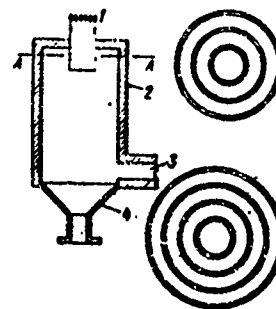


Figure 145. Diagram of reactor for burning titanium tetrachloride in an oxygen-containing gas.

The titanium tetrachloride is usually introduced through the inner passage, and the oxygen and auxiliary gases (neutral or combustible) through the passages between the inner and outer tubes.

With external heating of the unit, it is proposed that the titanium tetrachloride be burned after heating the reaction chamber, usually to temperatures from 800 to 1100°C. It is reported that fine-grained pigment titanium dioxide can be obtained in this way.

Thus, according to one of the patents<sup>(8)</sup> with this orientation, nitrogen is run into a container with titanium tetrachloride that has been heated to 120°C, forming a vapor-gas mixture consisting of approximately equal parts of the two components. This

Footnote (8) is on page 740.

mixture and preheated air are passed simultaneously through a vertical reaction tube that has been heated externally to 1100°C. The process is regulated so that the reactor will be supplied with 1500 ml per cubic decimeter per minute of a vapor-gas mixture containing 500 ml of  $TiCl_4$  vapor to 1000 ml of air.

As they pass down through the reaction tube, the injected reagents interact with one another, forming titanium dioxide and chlorine. The titanium-dioxide product is used as a pigment without subsequent processing.

The patent literature contains references to the possibility of producing pigment titanium dioxide by reacting titanium tetrachloride with oxygen or air in other temperature ranges as well.

Thus, patent<sup>(9)</sup> refers to the possibility of obtaining titanium dioxide that meets pigment-industry specifications by heating a mixture of  $TiCl_4$  vapor and oxygen at temperatures from 400 to 800°C. Patent<sup>(10)</sup> also recommends that the process be carried out in about the same temperature range. Before injection into the reactor, the reagents are preheated so that the reaction-chamber temperature will be 400-925°C when they are mixed.

The reagents are introduced in two parallel streams through concentric passages; the titanium chloride enters through a central passage 1-10 mm shorter than the outside passage. The ratio of the oxygen and titanium tetrachloride stream velocities should be about 0.15:1.

In another patent<sup>(11)</sup>, the titanium tetrachloride and oxygen, which have first been heated separately to temperatures from 1000 to 1100°C are admitted into a reaction chamber whose temperature is held at the 750°C level by use of an external cooling jacket. The  $TiCl_4$ -oxygen ratio recommended is 1:4. A combustion torch forms during the process where the preheated reagents emerge, and the titanium-dioxide smoke is released at the opposite end of the reaction apparatus.

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Footnotes (9), (10) and (11) are on page 740.

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As we noted previously, heat can be supplied to the reaction apparatus not only by external heating, but also by including some combustible gas (carbon monoxide, illuminating gas, hydrogen, etc.) in the vapor-gas reaction mixture. In this case, the reactant-preheating temperature is lowered sharply or no preheating is required at all. However, the amount of the combustible gas injected into the reaction mixture must be monitored carefully to prevent overdilution of the chlorine present in the exhaust gases. When combustible gases are injected, the titanium tetrachloride usually "burns" in a torch at the exit from the nozzle.

For example, titanium tetrachloride can be burned directly in a mixture of air with purified illuminating gas.<sup>(12)</sup> The result is formation of a finely dispersed titanium dioxide that is carried away with the gas stream and separated from it by means of appropriate filtering materials or electrostatic filters.

When carbon monoxide is used as the combustible gas, the required reactant-preheat temperature can be reduced to 300°C or lower. According to patent<sup>(13)</sup> all reaction components, including the combustible gas, are introduced through a nozzle formed by combining three concentric tubes, the outermost of which is chamfered toward the nozzle axis at the end that extends into the apparatus. The reagent mixture ( $TiCl_4$  and oxygen) is fed through the inner tube, the combustible gas through the intermediate tube, and the oxygen-containing gas through the outer tube (see Fig. 149). Good results have been reported for the following technological regime. A mixture of 1 part by volume of  $TiCl_4$  vapor with 1.3 parts by volume of oxygen is admitted to the reactor through the central tube at an exit velocity of 20 m/s after heating to 120°C. One part by volume of carbon monoxide is admitted through the intermediate tube at a speed of 4 m/s, and 0.5 part by volume of oxygen through the outer tube at 5 m/s. It is reported that the flame forms at about 1 cm from the nozzle under these conditions and that the reaction produces finely dispersed titanium dioxide; the yield is of the order of 99%.

Footnotes (12) and (13) are on page 741.

There are also other proposals for production of the dioxide by burning  $TiCl_4$  in the flame of a combustible gas;<sup>(14)</sup> in some of them, water vapor or hydrogen, which combines with oxygen to form water, is introduced into the reaction mixture.<sup>(15)</sup> The components of the vapor-gas reaction mixture also enter the reactor through three concentric tubes, as follows: titanium tetrachloride vapor through the inner tube, combustible gases through the middle tube, and oxygen with the water-vapor additive (0.005% by volume) through the outer tube. A mixture of equal volumes of carbon monoxide and hydrogen is used as the combustible gas. According to the patents, the titanium dioxide is formed as a finely dispersed product.

An American patent<sup>(16)</sup> recommends introducing the oxygen into the reactor in two streams - through a separate nozzle passage and in combination with titanium tetrachloride - to obtain high dispersion of the titanium dioxide product. The total amount of oxygen must be enough to convert all of the  $TiCl_4$  to the dioxide and burn all of the carbon monoxide. It is recommended that the latter be taken in amounts of 0.25-1 mole per mole of titanium tetrachloride. It is also reported that formation of a finely divided product is helped by diluting the vapor-gas mixture with a neutral gas (such as nitrogen) and by adding small amounts of water to the gases that are injected into the reactor separately from the titanium tetrachloride (oxygen, carbon monoxide, neutral gases).

However, it must be noted that inclusion of water in the initial vapor-gas mixture (above a certain critical content) causes difficulty in maintaining the process because of the rapid formation of titanium-dioxide buildups formed at the exit from the nozzle on contact between the water vapor and titanium tetrachloride. These buildups may block the nozzle orifices partly or even completely and, consequently, stop the process.

The permissible moisture content in the starting mixture for freedom from buildups on the nozzle depends on the velocity at which the gas streams leave the nozzle and on their preheat

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Footnotes (14, (15) and (16) are on page 741.

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temperature. It has been reported<sup>(17)</sup> that the permissible moisture content must be below 0.2% by volume even when the components of the starting vapor-gas mixture leave the nozzle at very high velocities, e.g., above 50 m/s. At lower velocities, e.g., between 5 and 20 m/s, the maximum moisture content should be about 0.05% by volume. These figures apply to the concentric technique for injecting the reagents and reagent temperatures from 100 to 300°C. At higher preheat temperatures, the moisture content in the vapor-gas mixture must not exceed 0.01% by volume, a figure at which the process can continue for a long time without buildup formation.

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It must also be remembered that when water additives are present in the vapor-gas mixture, and when hydrogen or a mixture of hydrogen with carbon monoxide is used as the combustible gas, the reaction will produce HCl as well as chlorine, which cannot but make the use of these gases difficult and complicate the design of the process equipment (by narrowing the choice of corrosion-resistant materials). Among the combustible gases enumerated as inert with respect to titanium tetrachloride, therefore, preference must be given to carbon monoxide, since no hydrogen chloride is formed as a byproduct.

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Along with the above versions of the process, a number of proposals call for combustion of  $TiCl_4$  in a "fluidized bed" to produce titanium dioxide.<sup>(18)</sup> The principle is as follows: the titanium tetrachloride is reacted with an oxygen-containing gas in a continuous process in a fluidized bed of inert solid materials that resist attack by  $TiCl_4$  and chlorine at high temperatures. Such materials might include, for example, oxides of silicon, aluminum, zirconium, or titanium with particle sizes from 40 to 1000  $\mu m$ , and the temperature of the bed, which also acts as an intermediate heat carrier, should be held in the 700-1300°C range (900-1100°C is preferred).

Even though the reaction of titanium tetrachloride with oxygen is exothermic, additional heat must be supplied to the bed

Footnotes (17) and (18) are on page 741.

from the outside if the process is run on a small scale. This can be done in several ways: external heating (which is, however, complicated in practice), introduction of a certain amount of a combustible gas (carbon monoxide) into the reaction mixture, preliminary heating of one or both reagents.

The amount of heat to be supplied externally depends on the scale of the process, decreasing with increasing productivity.

In the actual process, the titanium tetrachloride vapor and the oxygen-containing gas - either separately or after preliminary mixing (at a temperature below 500°C, so that the rate of their interaction will be practically negligible) - are passed through a set of inlets in the bottom of the reactor into a "fluidized bed," which must be deep enough to permit a practically complete reaction. The dust-gas mixture produced as a result of the reaction is ducted out at the top of the reactor. The solid phase, which is composed of pigment titanium dioxide, is separated from it (in cyclones, sleeve or electrostatic filters), while the chlorine (usually after preliminary concentration) is recycled for chlorination of the starting titanium-containing raw material.

When titanium tetrachloride is "burned" in a "fluidized bed," some grain-size classification of the titanium-dioxide product takes place. While the finer titanium dioxide, which is entrained by the ascending gas current, yields a product suitable for pigment applications, the coarser part of the dioxide is trapped in the "fluidized bed," where it usually adheres to the inert "bed" material. If this adhesion is too strong, it will not only lower the yield of pigment product substantially, but also make the "fluidizing" process itself much more difficult. Thus the patent literature indicates that this adhesion may not be allowed to exceed 20% of the mass of the inert solid material, which must be replenished periodically. However, the used solid material may be recycled after regeneration (removal of the titanium dioxide from it by chlorination).

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It is not particularly difficult to obtain a homogeneous "fluidized bed" in small units.<sup>(19)</sup> However, as the size of the equipment increases, it is necessary to feed the reactants into the "fluidized bed" through a set of inlets distributed around the lower horizontal cross section of the reactor in order to ensure uniformity of the bed. A reactor for production of titanium dioxide by burning  $TiCl_4$  in a "fluidized bed"<sup>(20)</sup> is shown schematically in Fig. 146.

The overwhelming majority of patents give no information on the crystal structure of the titanium dioxide formed. Only a few patents make reference to this question, noting that combustion of titanium tetrachloride in oxygen usually produces a mixture of the anatase and rutile modifications of titanium dioxide. Thus, according to Richmond,<sup>(21)</sup> when  $TiCl_4$  is reacted with oxygen at  $1000^\circ C$ , the product contains about 40% of the rutile form. The rutile content in the product increases when the process is conducted at higher temperatures;<sup>(22)</sup> however, the grain size of the product is then increased.

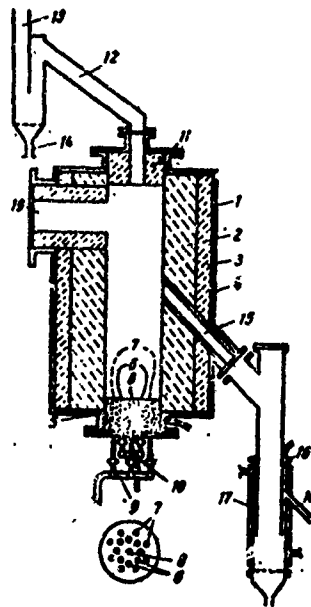


Figure 146. Reactor for titanium dioxide production by burning titanium tetrachloride in a "fluidized bed." 1) Shaft chamber lined with chlorine-resistant brick 2; 3) insulating brick; 4) steel shell; 5) ceramic block with passages for admission of titanium tetrachloride 6 and oxygen-containing gas 7 and 8 (which arrive via gas lines 9 and 10); 11) ceramic "plug" with passage for charging furnace with inert solid material, which arrives through pipe 12 from steel feeder 13 (to which compressed air is fed through pipe 14); 15) pipe for "decanting" inert solid material of "fluidized bed" into steel container 16 with water jacket 17 and "overflow" pipe 18; 19) gas line for tapping dust and gaseous reaction products from unit.

Footnotes (19), (20), (21) and (22) are on page 741.

The occasional references made in the patent literature indicate that certain additives must be introduced into the reaction chamber together with the principal components in order to guarantee the formation of pigment titanium dioxide with the rutile structure when  $TiCl_4$  is burned. It is reported that this also increases the rate of the process by forming crystallization nuclei in the vapor-gas mixture. According to available patent information, a considerable increase in the rate of reaction between the titanium tetrachloride and the oxygen-containing gas and production of titanium dioxide in the rutile form result when lower titanium chlorides<sup>(23)</sup> or aluminum chloride<sup>(24)</sup> is introduced into the reaction mixture.

When aluminum chloride additives are used in the combustion of titanium tetrachloride to obtain a product with the rutile structure, it is recommended that they be added to the reaction mixture in amounts such that the product will contain 0.5-5% (by mass) of  $Al_2O_3$ .<sup>(25)</sup>

To obtain pigment titanium dioxide in the form of a rutile product, Frey<sup>(26)</sup> recommends that combined additives - mixtures of aluminum and silicon chlorides - be added to the vapor-gas mixture just before combustion.

The expediency of adding volatile aluminum and silicon compounds in combination can be explained as follows. Aluminum chloride, although it has a rutilizing effect, i.e., contributes to the formation of titanium dioxide of the rutile structure during combustion of the  $TiCl_4$ , does not help improve particle-size uniformity. Additives of silicon tetrachloride, on the other hand, while exerting an antirutilizing influence during  $TiCl_4$  combustion (i.e., tending to form dioxide of the anatase structure), simultaneously improve the particle-size uniformity of the product. Aluminum chloride is superior to silicon chloride as regards the effect on the structure of the titanium dioxide produced. Thus the introduction of combined aluminum-chloride-silicon-chloride additives in combustion of titanium tetrachloride

Footnotes (23), (24), (25) and (26) are on page 741.

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may help produce a material with the rutile structure and uniformly fine particle sizes.

In this particular case,<sup>(27)</sup> it is recommended that these additives be introduced in amounts such that the final product will contain 0.5-3% (by mass) of  $Al_2O_3$  and 0.5-2% (by mass) of  $SiO_2$ . The process has the reaction zone supplied continuously with titanium tetrachloride vapor and oxygen-containing gas, around which an annular gas stream is formed by auxiliary gases, which consist of separately injected carbon monoxide and oxygen-containing gas. The auxiliary gases, forming an annular flame around the reaction mixture as the carbon monoxide burns, raise the temperature to the level necessary for the reaction between oxygen and titanium tetrachloride, which burns in a torch. The author of the patent claims that when the above aluminum- and silicon-chloride additives are included in the reaction mixture and the combustion-process temperature is 1000-1300°C, the result is a finely dispersed product that contains 90% of rutile.

If, however, silicon chloride alone is introduced into the reaction mixture [in amounts such that the final product will contain 0.5-2% (by mass) of  $SiO_2$ ] and the temperature of the titanium tetrachloride combustion reaction is 900-1000°C, dioxide of the anatase structure is formed.

It has also been proposed that titanium tetrachloride be burned in the presence of water vapor in order to obtain titanium dioxide with the rutile structure.<sup>(28)</sup>

Parallel streams of two vapor-gas mixtures that have been preheated to 800-900°C are fed into the reaction chamber: titanium tetrachloride diluted with an inert gas and air mixed with water vapor (from 2 to 70% referred to the oxygen content).

Proposals for simultaneous introduction of a mixture of oxygen and water vapor (or hydrogen) into the reaction mixture have the important shortcoming mentioned earlier: formation of HCl along with the chlorine, with the resulting undesirable chlorine

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Footnotes (27) and (28) are on page 741.

losses, difficulty of recycling the chlorine, and restriction of the choice of structural materials.

These disadvantages resulting from partial formation of HCl can be eliminated by using aluminum chloride and lower titanium chlorides instead of water vapor as additives in the combustion of titanium tetrachloride.

To obtain high-grade, finely dispersed titanium dioxide by burning  $TiCl_4$ , a great deal of attention must be given to eliminating or reducing factors that promote recrystallization of the dioxide and enlargement of its particles. Ensuring that the reaction will take place at a high rate and eliminating contact between the vapor-gas mixture and the reactor walls are of prime importance here, since titanium dioxide deposited on the walls has a coarse-grained structure and is not suitable for production of high-grade pigments.

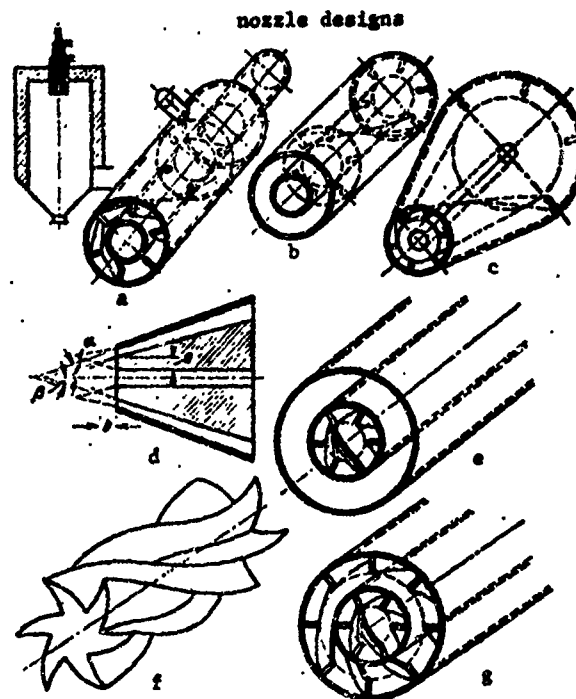


Fig. 147. Certain proposed nozzle designs for rapid mixing of starting components injected into reactor.

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To obtain a high rate of reaction between the titanium tetrachloride and the oxygen-containing gas, it is necessary to bring the vapor-gas components (which are usually preheated) up to the reaction temperature quickly. At the same time, process conditions must provide for the fastest and most complete mixing possible, so that the time spent by the reactants in the reaction zone will be minimized. Some proposals call for high-speed injection of the reactants at right angles to one another or head-on, and that a rotary motion be imparted to one of the components at exit from the nozzle.

Certain nozzle designs that have been proposed for rapid and thorough reactant mixing<sup>(29)</sup> are shown in Fig. 147. All of these nozzles can be used in the ordinary typical reactor shown at the top of the figure.

Figure 147a shows a nozzle with two concentric reactant inlets, the outer one of which is partitioned by spiral walls into a set of passages inclined to the central axis of the nozzle. These passages are connected by an annular pipe parallel to the central axis. A swirling motion, which will be faster the steeper the spiral (helical) surface, is imparted to the gas passing through the outer inlet.

The partitions may be extended to the walls of the central tube, thus leaving no intermediate space through which the passages communicate. They can also be cut off short of the nozzle exit orifice, i.e., the gas already in rotary motion may pass through an unpartitioned length of the supply tube, so that the rotational motion becomes more uniform.

Figure 147b shows a nozzle with an outer supply tube that is not partitioned at the end.

Figures 147c and d show a nozzle design that differs from Fig. 147a in that the central cylindrical passage is surrounded by two conical surfaces with the vertex of the cone in front of the nozzle exit orifice (Fig. 147d). The rate of reactant mixing

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Footnote (29) is on page 741.

can be regulated by varying the angles  $\alpha$  and  $\beta$  of the conical surface (they may also be equal to one another). In addition, with the proper geometrical dimensions (angles  $\alpha$  and  $\beta$ , distance  $a$ ; see Fig. 147d), the gas streams can be detached from the nozzle to impinge at a distance  $b$  from its end plane.

Figure 147e shows a nozzle in which the central delivery tube is partitioned by spiral walls into a set of passages that are out of parallel with the nozzle central axis. The partitions do not extend as far as the central axis, so that the common passage has a spiral configuration.

Figure 147f shows a helical element that can be inserted in the central orifice of the nozzle to divide its walls into a set of spiral passages.

Figure 147g shows a nozzle in which the passages are partitioned by several spiral walls into passages that do not run parallel to the nozzle central axis.

The duplex nozzles shown in Fig. 147 are designed for processes run without use of an inert gas. If, on the other hand, the titanium tetrachloride is to be burned in the presence of an inert gas, triplex nozzles based on the same principle can be used.

Other authors have also recommended the use of special technological devices in order to obtain a finely dispersed product by burning titanium tetrachloride. Thus, it is recommended in patent<sup>(30)</sup>, on the basis of small-scale laboratory experiments, that the titanium tetrachloride first be mixed with a small amount of an aromatic organic compound such as benzene before it is admitted to the reactor. As usual, the patent formula is vague when it comes to details of the process. It is stated only that finely dispersed titanium dioxide can be obtained by reacting a mixture of titanium tetrachloride and 0.01-20% (mol.) of benzene with an oxygen-containing gas taken in molar ratios from 1:1 to 1:10 (usually below 1:3) at 700-1500°C after preheating it to

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Footnote (30) is on page 741.

500-1000°C. It is recommended that the mixture of  $TiCl_4$  with benzene or a chlorinated derivative thereof (mono-, di-, or trichlorobenzol) be introduced through the internal passage of a concentric burner and the oxygen-containing gas through its external passage in the actual process.

The mechanism by which these additives exert their influence has not been studied. It may be assumed that on decomposing in the reaction zone, the aromatic organic compounds form centers of crystallization that help reduce the particle size of the titanium dioxide product. The chlorine obtained as a result of combustion contains HCl (the amount depending on the size of the aromatic additive), and this is undesirable.

A number of patent references indicate that the titanium dioxide that forms on combustion of titanium tetrachloride may clog the reaction chamber and obstruct the orifices of the nozzle through which the components of the starting vapor-gas mixture are supplied. The danger of buildups becomes particularly acute when the reagents go into strongly turbulent flow.

To eliminate this effect and the possibility of formation of a coarse-grained product during combustion of  $TiCl_4$ , it is necessary to move the reaction zone farther from the nozzle and the walls of the apparatus. For these purposes, most patents recommend that the reagents be injected into the apparatus through a nozzle with concentric tubes, using the central nozzle tube for the titanium-tetrachloride vapor, as we have already noted, the vapor is insulated from the reaction-chamber walls by a curtain of oxygen-containing gas or an auxiliary inert gas, of which a large excess is supplied. To reduce the danger of deposition and growth of titanium dioxide crystals at the tetrachloride inlet, patent<sup>(31)</sup> proposes that a nitrogen atmosphere be set up around the  $TiCl_4$  as it is introduced through the central nozzle orifice.

If the apparatus is large enough, contact between unreacted titanium tetrachloride and the reaction-chamber walls and,

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Footnote (31) is on page 741.

consequently, deposition of titanium dioxide on the walls can be eliminated.<sup>(32)</sup>

The same result can be obtained by admitting the  $TiCl_4$  vapor and oxygen into a vertical cylindrical reactor on the counterflow principle, in such a way that the chlorine formed as a result of the reaction will envelop the zone into which the titanium tetrachloride is admitted.<sup>(33)</sup>

The use of chlorine to protect the walls of the reaction chamber from deposition of the reaction product is also recommended in one of the later patents awarded to DuPont.<sup>(34)</sup> In this patent, the reaction-chamber walls are protected from contact with the reagents and the reaction product by a protective envelope of a chlorine-containing gas, which is formed by slow, steady diffusion of the gas from an external source into the reaction zone through a porous wall made from a refractory material (such as graphite) and held at a temperature of 500 to 800°C. This wall must be capable of reacting in the presence of chlorine with the  $TiO_2$  film that forms on it and do so in such a way as to regenerate titanium tetrachloride. It is recommended that the ratio of the mass of chlorine passed through this porous partition to the chlorine formed as a result of  $TiCl_4$  oxidation be held in the range from 0.1 to 1.

The apparatus used by the authors of the patent is shown in Fig. 148. A tubular reactor 3 made from a corrosion-resistant material and provided with inlet and outlet holes 4 and 5 is placed in a vertical furnace 1 with heated chamber 2. The reaction zone 6, whose walls 7 (porous graphite) represent an extension of the walls 8 and 9 of reactor 3, lies at about mid-length of the tubular reactor. A second tubular element 10 made from a corrosion-resistant metal or some other material (the patent does not indicate which other material) is placed directly above the porous wall of reaction zone 6; it has an inlet 11 in communication with the concentric passage 12, which terminates in the circumferential-slot inlet nozzle 13. The porous wall 7 of

Footnotes (32), (33) and (34) are on page 742.

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reaction zone 6 is enclosed by a concentric cylindrical element 14, which is made from corrosion-resistant material and has an inlet orifice 16 and forms passage 15. Oxygen (or oxygen-containing gas) and titanium tetrachloride are admitted to reaction zone 6 through inlets 4 and 11, and a protective gas (such as chlorine) enters through orifice 16 at elevated pressure, entering the reaction zone through the porous walls and dislodging from them any titanium dioxide particles that have been formed as a result of the reaction.

Other patents indicate that sintered silicon carbide, alundum, unglazed calcined kaolin, and certain other materials may be used to make the porous corrosion-resistant lining (wall) of the reaction vessel; of these materials, alundum is preferred because of its ready availability, ease of shaping, heat resistance, and anticorrosion and mechanical properties. For example, this material is recommended by the authors of patent<sup>(35)</sup>, who propose a process in which titanium tetrachloride is burned in oxygen and the titanium dioxide that forms is blown away from the refractory walls of the apparatus by a neutral gas. This gas might be nitrogen, chlorine, CO, CO<sub>2</sub>, or any of certain other gases.

When carbon monoxide is used, its reaction with the excess oxygen results in formation of CO<sub>2</sub>, a neutral gas that protects the surface of the reactor wall. For this purpose, the porous refractory walls of the reactor are fitted with a gastight jacket into which protective inert gas is fed under a small excess pressure to diffuse into the reaction chamber. Figure 149 shows equipment for implementing this process (which can be run either with or without CO as a combustible gas). Concentric triplex

Footnote (35) is on page 742.

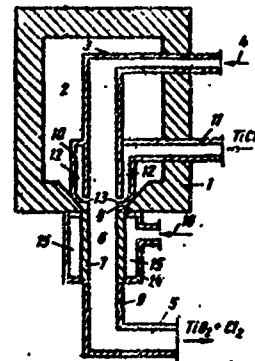


Figure 148. Apparatus for production of titanium dioxide from titanium tetrachloride (with dioxide particles blown away from reaction-zone walls).

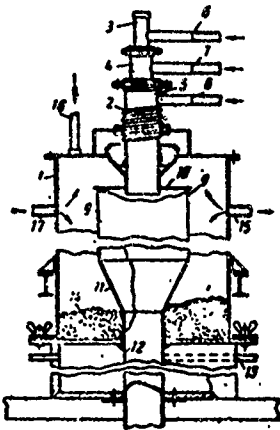


Figure 149. Apparatus for burning titanium tetrachloride (using a combustible gas and flushing of the titanium dioxide from the walls).

nozzle 2 is threaded into the steel casing 1 to supply the starting components to the reactor: titanium tetrachloride through 6 and 3 (by itself or with part of the oxygen), carbon monoxide through 7 and 4, and oxygen through 8 and 5. The reaction zone of the apparatus is a porous alundum cylinder 9 with alundum cover 10, which holds nozzle 2, and porous tapered bottom element 11 and outlet pipe 12 with alundum heat insulation 14. Casing 1 is supplied through pipes 15, 16, and 17 with the neutral gas, which flushes titanium dioxide particles off the porous alundum walls of the reaction zone as it passes through them. The dust-gas mixture produced by the reaction is

injected with cold gas through pipe 13 and the bottom of pipe 12 to lower its temperature; it is then ducted out of the unit and the titanium dioxide is separated from it.

Although the above measures make it possible to reduce considerably the possibility of contact between the  $TiCl_4$  vapor and the heated walls of the reactor, they do not eliminate such contact completely. As a result, titanium dioxide films may still build up gradually in the apparatus and adhere to the inner surfaces of the reaction chamber when  $TiCl_4$  is burned in an oxygen-containing gas at high temperatures.

Various methods may be used to remove these deposits from the apparatus. Thus, one of the patents<sup>(36)</sup> recommends that the combustion process be interrupted periodically as necessary and that the deposited titanium dioxide layer be removed by running a mixture of chlorine and carbon monoxide through the unit at 900-1200°C.  $TiCl_4$  and  $CO_2$  are formed and removed as a result of

Footnote (36) is on page 742.

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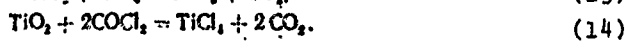
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The patent also indicates the possibility of removing deposited titanium-dioxide crusts by using other carbon-containing chlorinating agents in the appropriate temperature range (800-1350°C), such as  $\text{CCl}_4$  or  $\text{COCl}_2$ , which react with  $\text{TiO}_2$  in accordance with the equations



As a way of preventing formation of titanium-dioxide build-ups on the inner walls of the reactor, it has been suggested that water-cooled breakers be used to clean the unit mechanically without dismantling,<sup>(37)</sup> or that the reactor be made with a flexible inner wall to prevent  $\text{TiO}_2$  deposition.<sup>(38)</sup>

These specific difficulties encountered in the combustion of titanium tetrachloride to produce the dioxide become greater as the scale of the process is increased, partly because of the need to introduce large quantities of reactants through the nozzle.

There are two possible ways of introducing large volumes of titanium tetrachloride vapor into an industrial reactor: using a large-diameter inlet pipe or using a very high vapor flow velocity (in a small-diameter pipe). In the former case, a substantial amount of time is required for the inner layers of the titanium tetrachloride enter into the reaction (since they mix with the concurrently injected oxygen-containing gas at a slow rate), and this results in an unacceptable but inevitable increase in the grain sizes of the titanium dioxide produced. In the latter case, in which the titanium tetrachloride is introduced at a high flow velocity, its kinetic energy is so high that it penetrates the reaction chamber to a considerable distance before beginning to react with the oxygen-containing gas. To give the reactants time to react, it would be necessary to increase

Footnote (37) and (38) are on page 742.

the length (height) of the reactor substantially, and this would make it difficult to maintain the required high temperature in the reaction zone. However, even if the height of the reactor is increased to ensure complete reaction of all of the titanium tetrachloride introduced, it would still be necessary to extend the reaction time (i.e., the stay time of the reactants in the apparatus), and this would inevitably coarsen the grain of the titanium dioxide.

For combustion of titanium tetrachloride on an industrial scale, therefore, the conditions must be such as to permit continuous delivery of the reactants without obstruction of the feeder system, eliminate the possibility of deposition of the reaction product on the reactor walls, increase the reaction rate, reduce the dimensions of the equipment, and ensure acquisition of finely dispersed titanium dioxide. These objectives can be attained under industrial conditions by using not one, but several nozzles, including flattened designs. As we noted above, it has been proposed in the patent literature that one of the reagents be supplied along the axis of the apparatus, while the other is set in motion along a spiral path. This makes it possible to reduce the dimensions of industrial apparatus to technically acceptable proportions by stepping up the process and ensuring quick completion of the reaction. The vigorous mixing of the reactants also makes it possible to reduce the oxygen excess required for complete oxidation of the titanium tetrachloride.

However, it must be remembered that when this method is used to inject the starting components, their vigorous mixing increases the danger of obstruction of the inlet orifice by reaction products. To eliminate this, it is necessary to create conditions under which the gas streams will come into contact at a certain distance (of the order of several centimeters) from the inlet system. This might be done, for example, by using a relatively thick wall between two concentric reactant inlets. An intermediate inert-gas-filled zone might also be provided to separate the flows of the two reactants directly at the nozzle.

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The inert gas can be injected into the reaction space between the titanium tetrachloride and the oxygen-containing gas. Comparison of the various possible techniques for injecting these materials into the reactor indicates that preference should be given to central admission of the  $TiCl_4$  vapor so that it can be enveloped by the oxygen-containing and neutral gases.

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The rotation or spiral motion referred to above as necessary to step up the rate of industrial titanium tetrachloride combustion can be imparted to either of the reagents or to the inert gas or to both. This motion can be set up in the nozzle or after the nozzle, in the reaction chamber. For example, the gas might be set in rotation in the nozzle by inclined plates (vanes) inserted into it. Rotational motion might be set up directly in the reaction chamber by imparting such a strong spiral motion to the inert gas in the nozzle that its kinetic energy will be adequate to entrain at least one of the reactants, transferring the rotational motion to it.

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The patent literature contains certain information on methods of burning titanium tetrachloride in industrial-type units. Thus, one patent<sup>(39)</sup> describes the process in a reaction chamber 1.5 m in diameter and 3 m high. The starting components - titanium tetrachloride and oxygen - are preheated to 800 and 900°C, respectively, and injected into the reactor through a nozzle with concentric inlets; the cross-sectional area of the inner passage is 3 cm<sup>2</sup>, and that of the outer passage 4 cm<sup>2</sup>. The  $TiCl_4$  is introduced through the inner orifice at a rate of 8 moles/min, and the oxygen through the outer orifice at 25 moles/min with swirling in the nozzle. It is reported that this apparatus produces finely dispersed pigment titanium dioxide in 99% yield.

The literature offers practically no data on the performance of existing foreign industrial installations for titanium dioxide production by burning  $TiCl_4$ . There is only a very brief account [17] of work done toward production of titanium dioxide by this method at the Thann plant in France (Alsace). At this

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Footnote (39) is on page 742.

installation, the starting titanium-containing raw material is rutile, largely imported from Australia. The titanium tetrachloride obtained by chlorinating the rutile and appropriate purification is processed to the dioxide in accordance with the schematic flowchart shown in Fig. 150.

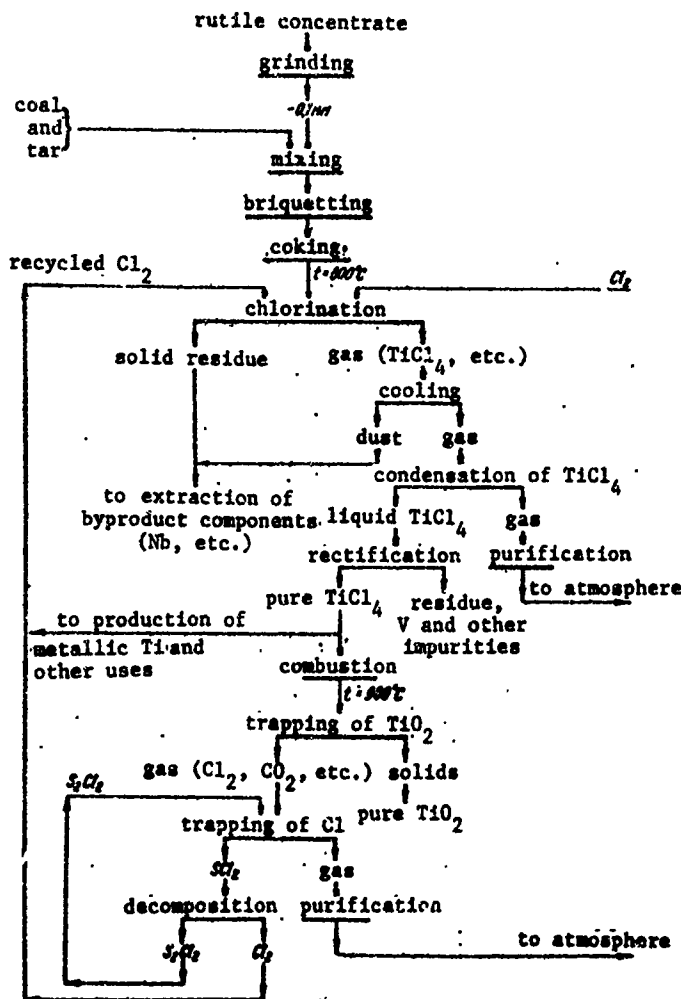


Figure 150. Schematic flow chart of titanium dioxide production from titanium tetrachloride at the Thann plant.

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The titanium tetrachloride is burned in a vertical cylindrical reactor into which it is fed in the liquid form through spray nozzles in the top of the apparatus. The combustion chamber is made of a molybdenum-containing chrome-nickel steel, but even then it is subject to considerable corrosion. The titanium tetrachloride is burned at a temperature of 900°C, which guarantees the desired structure in the titanium dioxide. Carbon monoxide and oxygen are fed into the reactor after dilution with air for temperature adjustment.

The titanium dioxide formed in the reaction is trapped on electrostatic filters, and the diluted chlorine (of which the exhaust gases contain about 20%) is sent for regeneration.

The chlorine is extracted from the exhaust gases by binding it to sulfur monochloride  $S_2Cl_2$  in the presence of iodine (about 0.001%) as a catalyst. The process is run at 220°C and a pressure of about 10 atm; its equation is



The resulting sulfur dichloride  $SCl_2$  is then decomposed by heating. This liberates the chlorine, which is returned to the production cycle for use in chlorinating titanium-containing raw material, and reforms the sulfur monochloride, which is returned to the process for reaction with dilute chlorine.

Although this process permits regeneration of the chlorine from its dilute mixtures, it is highly complex and expensive. American firms (DuPont and others) have published no information at all on the apparatus and technologies used in their industrial scale titanium-tetrachloride combustion processes. It has been reported only that the chlorine formed in the combustion of  $TiCl_4$  is recycled at the DuPont plants for chlorination of titanium-containing raw material, but it is not indicated how this is accomplished.

\* \* \* \* \*

Although these fundamental technological schemes for production of titanium dioxide from  $TiCl_4$  - aqueous-solution hydrolysis, hydrolysis in steam, and combustion in an oxygen-containing gas

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can produce a quality product, they are not, as we indicated above, equivalent.

The "wet" hydrolysis of titanium tetrachloride is unsuitable as a basis for economically profitable industrial production of titanium dioxide, since it does not permit use of the chlorine of the  $TiCl_4$  (of the order of 1.75 tons per ton of dioxide), which is irrecoverably lost in the form of dilute hydrochloric acid. The process is also burdened with substantial difficulties encountered in filtering the residues that precipitate out during hydrolysis.

The hydrolysis of titanium tetrachloride in steam has unquestionable advantages over the hydrolysis of this compound in aqueous solutions. Production flow becomes substantially simpler when titanium dioxide is made by the vapor-phase process. The operations of filtering, drying, and calcining the deposits become unnecessary, and less grinding of the product is also required, since it becomes a matter more of homogenization than of actual grinding. Finely dispersed, homogeneous pigment titanium dioxide can be produced by this method. It produces hydrogen chloride or hydrochloric acid in concentrations higher than that of the acid obtained in the aqueous-solution hydrolysis. Titanium dioxide can be produced in a continuous technological process based on this method. However, the vapor-phase method has a very serious shortcoming in the impossibility of obtaining chlorine simultaneously with the titanium dioxide for possible direct recycling for chlorination of titanium-containing raw materials; further, major difficulties arise in the attempt to find structural materials suitable for the industrial equipment, which must resist attack by HCl at high temperatures.

The process in which titanium tetrachloride is burned in an oxygen-containing gas retains the above positive features inherent to the vapor-phase method, but is free of its principal drawback. It permits setting up a closed chlorine cycle, with recycling of the gas for chlorination of the starting titanium-containing raw material; this makes this particular method of titanium dioxide production economically defensible. Combustion

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of titanium tetrachloride is a highly interesting process from the practical standpoint, since it can be used in a relatively simple technological flow for continuous production of high-quality titanium dioxide. The profitability of this process will make possible its introduction into the industry on a broad scale.

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|                                |  | 718                            |
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| 700                            | 1) The acid factor is the ratio of the mass concentration of "active" $H_2SO_4$ (the free acid plus the acid bound with titanium) to the $TiO_2$ concentration in the solution.  | 721                            |
|                                |  | 721                            |
| 701                            | 2) This system provides for the introduction of a small antimony-oxide additive into the suspension (about 1% on the $TiO_2$ ), with conversion of the $Sb_2(SC_4)_3$ formed in the reaction with sulfuric acid to $Sb_3S_3$ in subsequent operations by addition of sodium or iron sulfide. The antimony sulfide, which precipitates in the form of a bulky deposit, carried suspended particles with it and helps clear the titanium sulfate solution. | 723                            |
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Symbol List

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|    |  | ROLE   | WT | ROLE   | WT | ROLE   | WT |
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