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PRODUCTION AND PHYSICAL METALLURGY OF PURE METALS -- PART III

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PRODUCTION AND PHYSICAL METALLURGY OF PURE METALS -- PART III

Production of Ductile Hafnium by the Iodide Method

/Following is a translation of an article by V. S. Yemel'yanov, P. D. Bystrov and A. I. Yevstyukhin in Metallurgiya i Metallovedniye Chistykh Metallov (Production and Physical Metallurgy of Pure Metals), No. 1, Moscow, 1959, pages 63-69./

Like zirconium, metallic hafnium is greatly dependent in its mechanical properties on the quantity of admixtures. In particular, impurities in hafnium consisting of ordinary gases -- oxygen, nitrogen, hydrogen -- lead to a lower or even to a complete lack of ductility of the metal. In accordance with the above, ordinary metallurgical methods produce hafnium exclusively in the nonductile state.

At the present time, the only method to prepare malleable hafnium is by refining the metal by the so-called iodide method.

It is known that this method was widely used during the last decade for the industrial production of ductile titanium and zirconium. Dictated by practical needs, the most complete and systematic studies concerning the iodide method were carried out for the preparation of just these two metals. The preparation of ductile hafnium is based on the similarity in properties of hafnium and zirconium.

Nevertheless, a more detailed study of the refining of hafnium has a definite practical interest since even though hafnium and zirconium have much alike, the processes of their refining are somewhat different.

In particular, it is known (1), (2) that one-cycle refining in the majority of cases does not yield ductile hafnium if the initial metal was not degassed at temperatures of 800°C; whereas degassing of initial metal at temperature of 300-350°C, assures the preparation of very ductile zirconium rods. It is possible that the lower

ductility of hafnium (2) is not a property of this metal, but is merely the result of an incorrect selection of refining methods.

On the other hand, a detailed study of the conditions for the refining of hafnium permits more definite conclusions concerning the behavior of hafnium residues in the iodide refining of zirconium and indicates the possibility of an additional refining of zirconium from hafnium by an appropriate selection of refining procedure.

As it has been established by many research works covering zirconium (for instance (3), (4), the basic parameters which control refining are the pressure of iodide vapors inside the apparatus and the temperatures of the filament and (within certain limits) of the initial material. An important role is played in the course of refining by the binding of tetra-iodide into nonvolatile lower iodides. A study of the role of these factors during hafnium refining is the purpose of the present work. The results of temperature regimes for preparing iodide hafnium are given below.

Experimental Methods

Deposition of hafnium was carried out in a cylindrical flask, 4, of molybdenum glass 18 to 20 cm long with a diameter of 8 cm (Fig. 1). The initial tungsten filament, 5, with a diameter of 0.05 mm and about 8 cm in length was heated by an alternating current passed through molybdenum electrodes, 6, welded into the flask. The flask was provided with an ampoule, 3, the purpose of which was to achieve in the flask a certain pressure of hafnium tetra-iodide vapors (by means of maintaining the ampoule at a certain definite temperature lower than that of the flask itself). After the conclusion of the experiment the ampoule was welded off, and its iodide content was used for subsequent experiments.

Evacuation of the flask was effected through tube 1, into which the ampoule with iodide, 2, was inserted. The flask was welded off from the system after a vacuum of the order of 10^{-4} mm Hg was achieved at a temperature 30 to 50°C higher than that of the flask during the test.

The crude metal, 7, was placed during degassing in a quartz ampoule connected with the flask of tube, 8, and was heated to 800-850°C.

After degassing of the flask, it was filled with the initial metal. and the iodide was sublimated; whereupon the quartz ampoule and tube 1 were welded away.

During the experiment, the flask was heated by an electric resistance heater. The temperature of the flask itself and of the ampoule for iodide was measured by

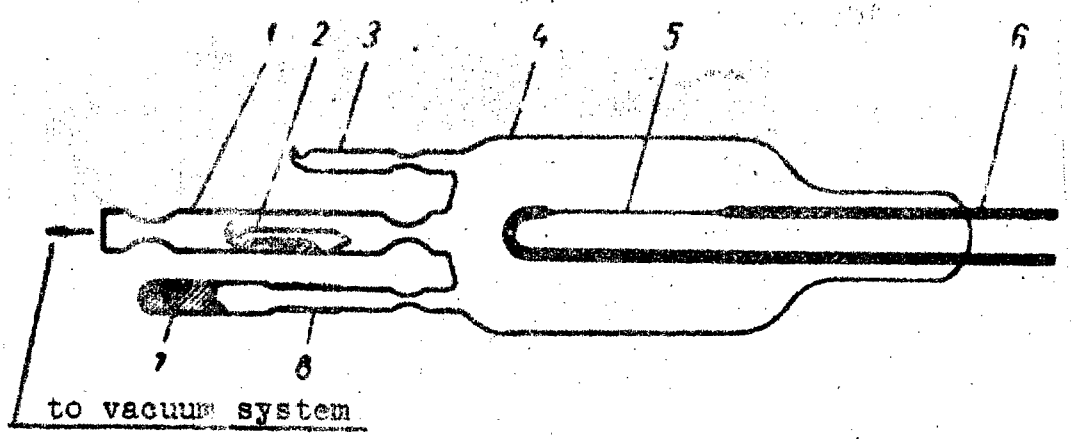

Fig. 1. Reactor flask prepared for its connection to the vacuum system.

standard platinum-platinum rhodium thermocouples. The filament temperature was measured by optical OPPIR-9 pyrometer; no correction was introduced for the radiation capacity of hafnium, and in all cases described below brightness temperatures are given. Absorption in tetraiodide vapors and in the glass of the flask was disregarded because of its low value.

The rate of metal deposition was characterized by the average rate of current increase through the filament in the range between 3 to 12 amps.

The initial metal used in all experiments was four-times refined iodide hafnium in rods with a diameter of about 2 mm and a typical weight of up to 35 g. Iodine was introduced in the form of hafnium tetraiodide, which after each experiment was almost completely sublimated into the ampoule, 3, and was used for subsequent experiments.

Preparation of Initial Metal

The initial material for the preparation of metallic hafnium oxide (HfO_2,96.27%; ZrO_2,3%; the content of other elements was inconsiderable except for Fe, 0.25%). The oxide was reduced in an iron crucible with calcium in the presence of $CaCl_2$ in an atmosphere of argon, according to the method described by Kalish (5). The metallic hafnium powder thus prepared was considerably contaminated with iron because of its high content in initial oxide and apparently also because of too high a temperature (1,100°C) of the reduction.

The elimination of iron was carried out by repeated refining of the prepared hafnium by the iodide method. In the course of the refining, iron is partially tied into a scarcely volatile (at a flask temperature of 300°C) iron iodide which is deposited on the walls of the flask near the initial metal, /and the iron/ partly remains at the surface of the initial metal and is eliminated by boiling in hydrochloric acid.

Rods of once-refined hafnium were rather brittle. It was now also found that the greater the diameter of the rod of iodide hafnium, the lower its ductility. Thus, rods with a diameter of 1 mm, prepared in the first experiment, showed some ductility and could be bent with a characteristic "tin crackling" around a radius of about 200 mm. Conversely, a rod of a 2.2-mm diameter was found to be as brittle as glass and broke under the lightest pressure.

Deterioration of iodide hafnium properties when the raw metal becomes exhausted is noted by other researchers (1). It was also found (2) that the degassing of the

initial metal at a temperature of 800°C produces ductile hafnium after one-cycle refining. In this connection, it was assumed that the low ductility of once-refined hafnium rods was caused by the transfer into iodide metal of the hydrogen contained in the initial metal.

However, the degassing of hafnium powder at 800°C, as carried out by us, did not lead to a noticeable improvement in the ductility of the iodide metal prepared. This /result/ causes us to believe that, in given cases, the brittleness of once-refined hafnium rods depends not on hydrogen but on the iron which together with hafnium, is partially transferred on to the filament. It is natural that the greater the diameter of the iodide metal rod, the greater the diameter of the iodide metal rod, the greater the transfer of iron, because of exhaustion of the raw metal and because of the increased flask temperature leading to a greater volatility of the iron iodide.

It is interesting to note that it was impossible to obtain rods with a diameter greater than 2.2 mm after a one-cycle refinement. The reason for /this limitation/ was the rupture of the filament in the course of the process. This /event/ consists in the phenomenon when glowing hafnium wire at a certain moment and without apparent reason is spontaneously ruptured in two or three pieces. No melted spots are found at the point of rupture. Undoubtedly, this phenomenon is related to the presence of considerable quantities of iron in once-refined hafnium, possibly also of the presence of other admixtures which concentrate at the interface of the hafnium crystals, weaken their cohesion and results in "red brittleness." This /hypothesis/ is proved by the fact that after a third and a fourth refining when relatively pure hafnium is deposited, ruptures were no longer observed.

As a result of preliminary refining, 35 g of four-times refined hafnium were prepared in the shape of a wire with a diameter of 1.5 mm, reminescent of iodide zirconium rods. This hafnium was rather ductile, for the rods could be bent to 180° with a radius of about 3 mm. This metal was used as the initial metal in the experiments which are described below and which cover different regimes of hafnium refining.

Dependence of the Hafnium Deposition Rate on the Pressure in the Apparatus and on the Temperature of the Initial Metal

In the experiments for the determination of the dependence of deposition rate on the pressure of hafnium

tetraiodide, 35 g of four-times refined hafnium and 1.5 g of hafnium tetraiodide were used.

The temperature of the filament was 1,350°C; the initial temperature of the flask and of the initial metal was 355°C; toward the end of the experiment the radiation of the filament raised the flask temperature to 370-375°C. The pressure of hafnium tetraiodide vapors in the flask was controlled by the temperature of excess tetraiodide concentrated in the ampoule, 3, (Fig. 1), and was maintained at a constant level.

The dependence of the metal-deposition rate on the tetraiodide vapor pressure (temperatures of the ampoule with iodide) is shown in Fig. 2. The maximum rate of the hafnium deposition of the filament takes place at approximately 230°C. The comparison of hafnium and zirconium (3) shows a very insignificant difference between the maximum rates of deposition of these metals.

The dependence of the hafnium deposition rate at the filament on the temperature of raw metal in the range between 270-475°C (the pressure in the flask remaining unchanged) was investigated under conditions set for the series of experiments as described above. However, now the ampoule temperature with excess iodide was the same in all tests (230°C); whereas the temperature of the flask itself with the initial metal placed in it was variable.

The results of tests are also shown in Fig. 2, and as in the case of zirconium (3) it was found that the temperature of the raw metal influences the rate of metal deposition to a considerably lesser extent that the pressure in the flask. A certain acceleration of the process at a higher temperature of the initial metal is probably due to an increased rate of diffusion and to an increased rate of interaction between the iodide and the initial metal.

Dependence of Hafnium Deposition Rate On Temperature Of Filament

The dependence of hafnium deposition rate on the filament temperature was tested at a flask temperature of 360°C and an iodide ampoule temperature of 230°C. The results obtained are shown in Fig. 3. Qualitatively the dependence observed is analogous to that of zirconium (3). Quantitavely the difference is quite considerable, for at the same filament temperature zirconium is deposited twice as fast as is hafnium.

Undoubtedly a considerable role is played by the difference in the diffusion coefficients of zirconium and hafnium tetraiodides, as well as by certain differences in

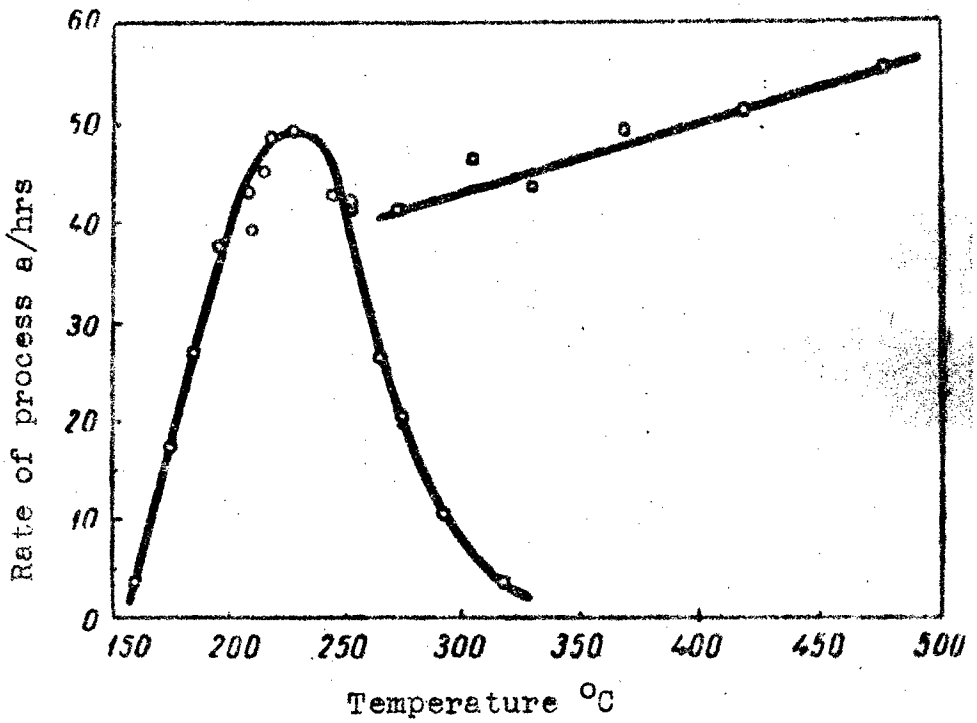

Fig. 2. Dependence of the metal-deposition rate on the temperature of the ampoule containing excess tetraiodide (curve with a peak) and on the temperature of the initial metal (straight line).

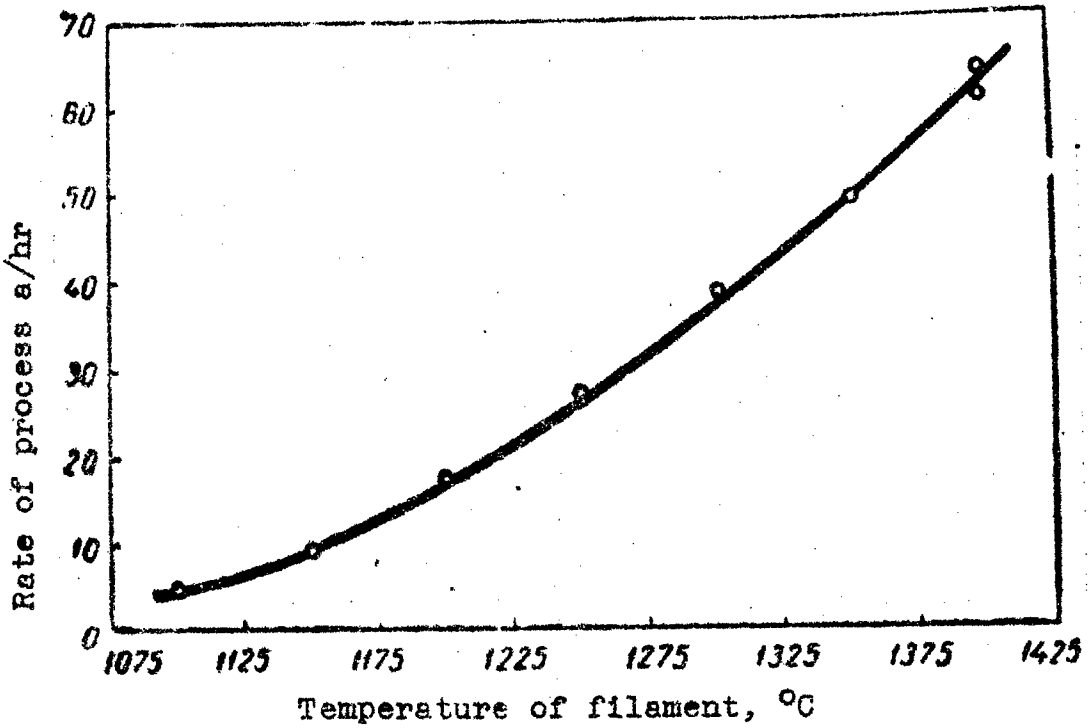

Fig. 3. Dependence of hafnium deposition rate on temperature.

the experimental conditions as per work (3) and in the experiments of the present work. The difference in the rates, however, is too great to be explained by the above mentioned circumstances alone. Very probably a considerable role is also played by the differences between the dissociation constants of zirconium and hafnium iodides. Indeed, one must assume that hafnium tetraiodide molecules are more stable than zirconium tetraiodide molecules, and that, therefore, the partial pressure of iodine around the filament is lower in the case of hafnium than in the case of zirconium. It is regrettable that this supposition cannot be proved thermodynamically because of the absence of accurate thermodynamical data covering zirconium and hafnium iodides.

Conclusions

As a result of iodide refining of hafnium under different regimes, it was established that

1. The dependence of the hafnium deposition rate on the temperature of the initial metal and on the pressure in the flask coincides with an analogous dependence for zirconium;
2. The dependence of the hafnium deposition rate on filament temperature also coincides qualitatively with a similar dependence for zirconium; the deposition rate for hafnium is however considerably lower;
3. The results obtained coincide, in general, with present data available, according to which no substantial separation of zirconium from hafnium takes place during the iodide process.

Because of the absence of accurate thermodynamic data concerning iodides of these metals, no final conclusion can be made as to the problem whether it is generally possible by somewhat modifying the refining process or by selecting a special regime to achieve the separation of hafnium during the zirconium refining process.

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Investigation Of The Process Of Obtaining Ductile Molybdenum By The Thermal Dissociation Of Its Pentachloride

/Following is a translation of an article by G. A. Leont'yev in Metallurgiya i Metallovedeniye Chistykh Metallov (Production and Physical Metallurgy of Pure Metals), No. 1, Moscow, 1959, pages 70-77./

Existing methods of molybdenum preparation from the gaseous phase (thermal dissociation of molybdenum hexacarbonyl in hydrogen (1), reduction of molybdenum pentachloride by hydrogen(2)) produce metallic coating with a higher degree of hardness /than heretofore./ This /result/ is explained by the fact that the coating during its growth is in contact with hydrogen introduced from the outside, in which harmful impurities may be present.

One could assume that the preparation of molybdenum by the thermal dissociation of volatile compounds when carried out in a contained volume would be more practical, as, in such a case, the growing metal does not come in contact with the walls of the apparatus or with outside gases. One must assume that the purer the volatile compound, the purer will be the prepared molybdenum.

If the volatile compound is a halide, its thermal dissociation is possible under the following conditions:

1. One must select a volatile compound dissociating noticeably at a temperature lower than that of the melting point of the metal being deposited;
2. The deposited metal must have a low vapor pressure at the dissociation temperature;
3. The halogen being released must be tied into a volatile compound at a possible low temperature;
4. At the temperature of formation of a volatile halide, the device must not be corroded or deformed.

We attempted to carry out the thermal dissociation with the purpose of obtaining ductile molybdenum, and the volatile compound taken for that purpose was molybdenum pentachloride $MoCl_5$.

This selection is not accidental. As far back as in 1909 Pring and Fielding (3) observed that if a carbon rod is heated in $MoCl_5$ vapors up to 1,300°, pure molybdenum is deposited on the rod (at temperatures above 1,300° molybdenum carbide is formed). Van-Arkel (4) in 1939 disclosed that very pure molybdenum is prepared by heating a molyb-

denum wire in an atmosphere of its pentachloride; whereas liberated chlorine must be bound by hydrogen or by molybdenum powder.

Having a certain experience in the iodide refining of titanium and zirconium, we decided to utilize this classical prescription of Van-Arkel for preparing pure molybdenum.

The essence of the process consists of the following: In the absence of air, tungsten or molybdenum wire is heated up to 1,300-1,400° in molybdenum pentachloride vapors (Fig. 1); whereupon thermal dissociation of the pentachloride takes place:

$$2MoCl_5 \longrightarrow 2Mo + 5Cl_2$$

Molybdenum is deposited on the filament, and the liberated chlorine, under favorable conditions, again reacts with the molybdenum introduced into the reactor for refining purposes and follows the reaction

$$2Mo + 5Cl_2 \longrightarrow 2MoCl_5$$

The volatile pentachloride formed touches the filament and dissociates at its surface.

This process satisfied all of the conditions as mentioned above.

1. As the volatile halide compound, molybdenum pentachloride $MoCl_5$ is used; it consists of black crystals with a melting point of 194° and a boiling point of 268° (5).

The vapor pressure of $MoCl_5$ at 194° is approximately 170 mm Hg (2), i.e. it is a sufficiently volatile compound.

2. At 1,530° the vapor pressure of molybdenum is $6.4.10^{-9}$ mm Hg (6), meaning that molybdenum is practically nonvolatile.

3. Chlorine reacts easily with molybdenum powder, forming $MoCl_5$. In our experiment, pentachloride formation was already observed at 130°, but the process was slow; when the temperature was raised to 250-300°, chlorination was considerably accelerated.

4. The glass apparatus showed sufficient resistance during the process.

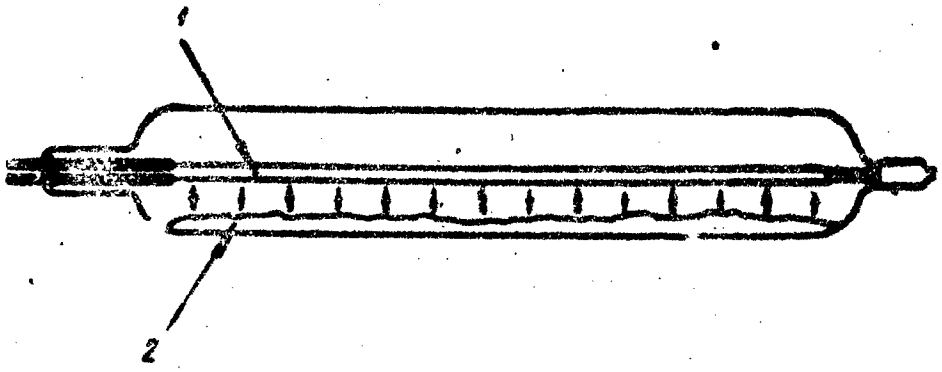

Fig. 1 Schematic diagram of thermal dissociation; 1. Dissociation of pentachloride on glowing filament following the reaction of $2MoCl_5 \xrightarrow{1,300^\circ} 2Mo + 5Cl_5$; 2. Interaction of raw metal with chlorine forming volatile pentachloride following the reaction $2Mo + 5Cl_2 \xrightarrow{300^\circ} 2MoCl_5$.

Selection of Methods For The Synthesis And Dissociation Of Molybdenum Pentachloride

It is expedient to introduce pentachloride into the reactor in welded ampoules. After the evacuation and sealing of such a device, the ampoule can be broken and molybdenum pentachloride can be charged into the reaction area. The presence of air in the chlorine during the synthesis of $MoCl_5$ results in the contamination of the pentachloride by oxychlorides.

At present, at least four molybdenum oxychlorides (7) are known (see table).

Molybdenum Oxychlorides

Formula	Molecular weight	Color	Behavior when heated
$Mo\ OCl_4$ oxytetrachloride	253.78	Green crystals when anhydrous	Sublimates
MoO_2Cl_2 oxychloride, di	198.86	white-yellow scale crystals	Sublimates
$Mo_2O_3Cl_5$ oxypentachloride, tri	417.19	Dark brown crystals when anhydrous	Sublimates
$Mo_2O_3Cl_6$ oxyhexachloride, tri	452.64	ruby-red or bright purple crystals	Decomposes

It is known that $MoCl_5$ reacts violently with the humidity of the air, forming molybdenum oxychlorides. Taking this/fact/ into consideration, we devised and carried out such an operation (Fig. 2) for preparing $MoCl_5$ which would exclude its contact with the air.

From 45-50 g of molybdenum powder we could obtain 125-140 g $MoCl_5$. For the elimination of oxychlorides, $MoCl_5$

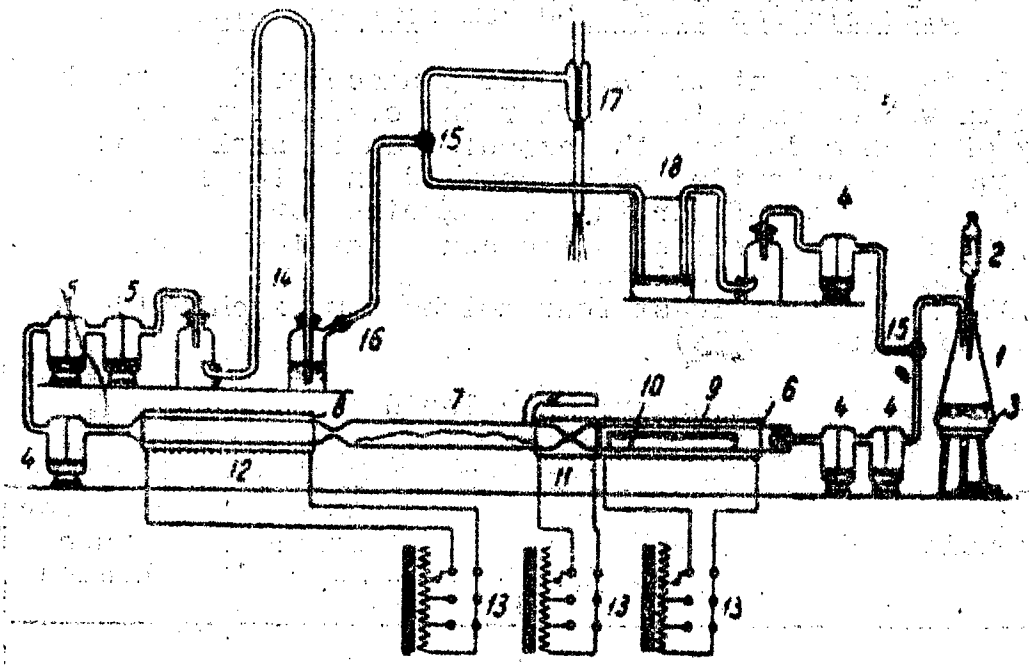

Fig. 2 Diagram of installation for preparing molybdenum pentachloride: 1 - chlorine generator; 2 - hydrochloric acid; 3 - potassium permanganate; 4 - scrubber with sulphuric acid; 5 - scrubber with caustic alkali solutions; 6 - pentachloride generator; 7 - pentachloride condenser; 8 - collector of pentachloride strongly contaminated by oxychloride; 9 - furnace for heating pentachloride generator; 10 - boat with molybdenum weighed portion; 11 - furnace for heating vacuum seal; 12 - furnace for heating pentachloride condenser at the beginning of chlorination; 13 - autotransformers controlling the temperature of furnaces; 14 - water lock preventing suction of air into the system; 15 - three-way valve; 16 - one-way valve; 17 - water suction pump for elimination of air and chlorine from the system; 18 - chlorine absorber at outlet from the system.

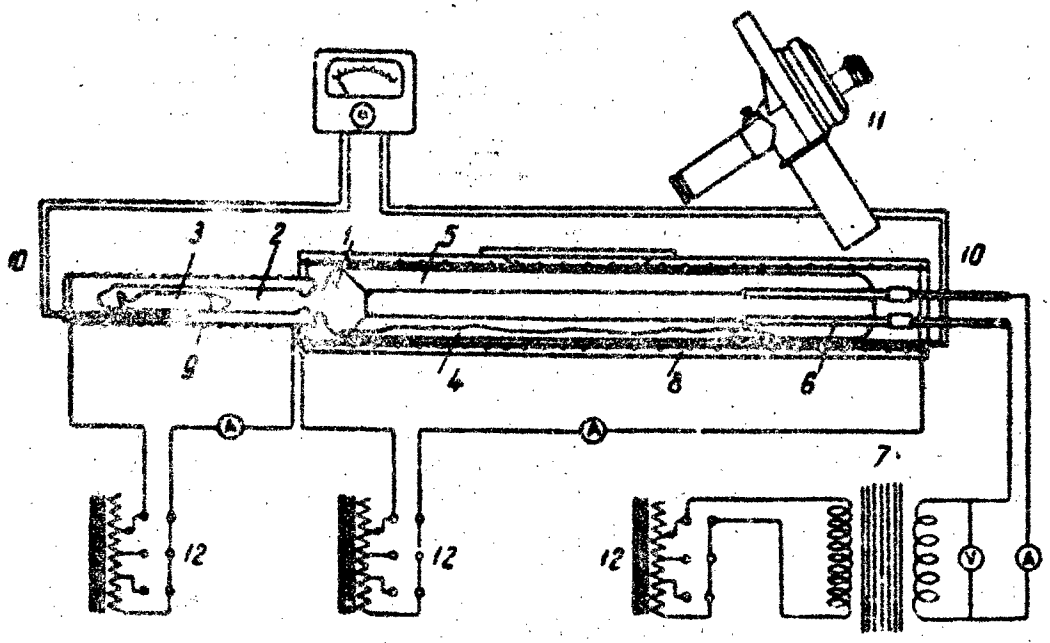

Fig. 3 Diagram of apparatus for the preparation of molybdenum by thermal dissociation: 1 - flask; 2 - neck of flask; 3 - ampoule with pentachloride; 4 - crude metal; 5 - filament; 6 - molybdenum leads; 7 - step-down transformer for filament heating; 8 - furnace for heating flask; 9 - furnace for heating its neck; 10 - thermocouples; 11 - optical pyrometer; 12 - autotransformers.

was distilled under vacuum and poured under vacuum into ampoules, which were welded. It was possible to collect 100-120 g $MoCl_5$ into ampoules. If these operations are carefully carried out, one obtains $MoCl_5$, which is black.

Very few data are available concerning the vapor pressure of $MoCl_5$. Childs and his colleagues give an approximate dependence between the vapor pressure P (mm Hg) and the absolute temperature T for $MoCl_5$ as follows:

$$P = 13.1 - \frac{5210}{T}$$

A graph plotted according to this equation shows that in the temperature range of 140-160° the vapor pressure increases from three to 10 mm Hg. Just this pressure range is used when refining zirconium by the iodide method. We decided to begin the study of the conditions of the deposition also using this pressure range.

Considering that the synthesis of $MoCl_5$ proceeds rapidly in the range of 250-300°, it becomes necessary to maintain different temperatures at different sections of the device; i.e., 140-150° near the ampoule with $MoCl_5$, and 250-300° near the molybdenum powder.

Therefore, the schematic diagram of the apparatus for deposition appears as shown in Fig. 3.

Into a steel flask (diameter 40 mm, length 380 mm) with a neck, molybdenum leads are welded in, to which a tungsten or molybdenum filament is affixed. The ampoule with $MoCl_5$ is placed in the neck of the device and is heated by a separate furnace. This /procedure/ enables the control of any pressure of molybdenum pentachloride vapors in the apparatus. 20-25 g of molybdenum powder are placed into the flask and are distributed uniformly beneath the filament.

The filament is supported by a molybdenum or quartz hook, so as to avoid its sagging.

Results Of Preliminary Tests

Tests have shown that the deposition takes place at the following temperatures: in the ampoule at 140°; in the body of the apparatus, 280-320°; at the filament, 1,280-1,380°.

The types of crystals prepared are shown in Fig. 4.

After each experiment, a light sediment of molybdenum trichloride $MoCl_3$ was observed on the walls of the apparatus. We carried out molybdenum deposition on wires of different diameters. It was found that optimum deposition takes place on a wire with a diameter of 0.49 mm or 0.2 mm. On a wire with a diameter of 0.1 mm the deposition was unsuccessful,

Fig. 4 [For legend see next page]

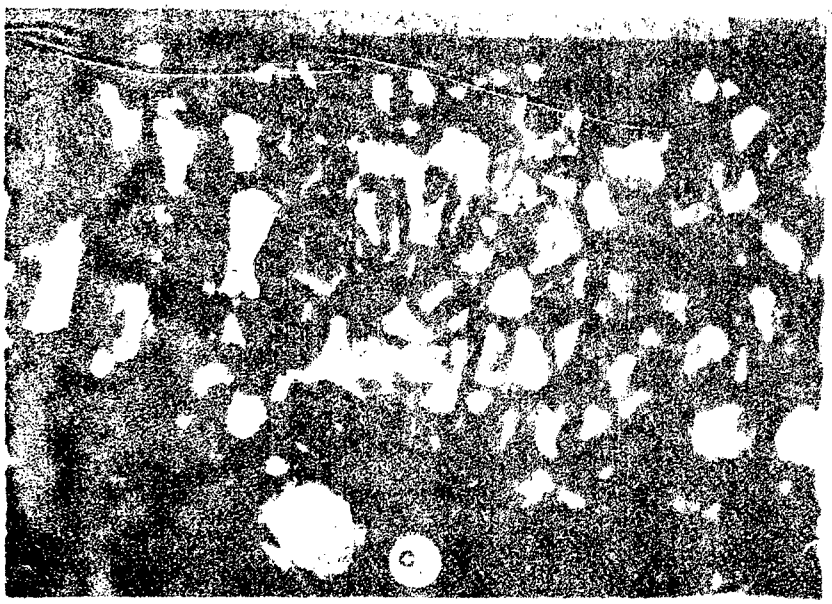

Fig. 1. Molybdenum crystals prepared by thermal dissociation of $MoCl_4$: a - rectangular, b - plate shaped, c - nonoriented (magnification 45 times).

because the wire dissolved rapidly.

Considerable difficulties were encountered in contacting the filament with molybdenum rods. This problem has not yet been solved and requires further study.

Further, it is difficult to suspend the filament so as to protect it from a contact with molybdenum powder when the filament sags. Molybdenum hooks dissolve. Quartz hooks are more resistant, but the influence of quartz on molybdenum rods being grown has not been determined. Special tests that were carried out to establish the balance of the operation have shown that the filament grows on behalf of the refined metal, whereas the $MoCl_5$ carries out the function of a metal transfer agent.

Here are some data covering the process as obtained by us in preliminary tests.

The initial current through the filament with 0.2 mm diameter was four amperes; whereas the final current when the filament grew to 1.2 mm diameter was 25 amperes. The voltage was 12 and seven volts respectively. The rate of growth in different tests varied from 4.1 to 16.8 a/hour. The microhardness of molybdenum crystals as measured on a PMT-3 instrument varied for different tests from 175 to 225 kg/mm^2; in separate crystals it reached 268 kg/mm^2.

Conclusions

1. The possibility of preparing molybdenum by the thermal dissociation of molybdenum pentachloride was confirmed.
2. Methods for preparing anhydrous pentachloride of molybdenum were worked out.
3. An apparatus having a rate of deposition up to 410 mc/hour was devised.
4. It was established that the crystallization of metal on the filament takes place on behalf of molybdenum placed at the bottom of the flask; whereas the introduced $MoCl_5$ is only a carrier of the metal.
5. The microhardness of the crystals obtained reaches 175-200 kg/mm^2, /a range of values/ which is lower than the microhardness of deposition obtained by the thermal dissociation of molybdenum carbonyl or from the reduction of molybdenum pentachloride by hydrogen.

This /result/ would seem to indicate that a thermal dissociation of $MoCl_5$ produces purer molybdenum.

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Investigation Of The Iodide Process For Producing Zirconium, Employing Zirconium Carbide As Raw Material

/Following is a translation of an article by A. I. Yevstuyukhin, I. P. Barinov and D. D. Abanin in Metallurgiya i Metallovedeniye Chistykh Metallov (Production and Physical Metallurgy of Pure Metals), No. 1, Moscow, 1959, pages 78-83./

The cost of iodide zirconium is very high, since metallic zirconium prepared by other methods is used in the iodide refining process. Therefore, the prospect of preparing iodide zirconium from a cheaper raw product, such for example as zirconium carbide, is attractive. In the literature there are indications concerning attempts of carrying out a similar process with titanium carbide(1), but their results were not described. The object of the present work was to verify experimentally this possibility.

Reaction Of Zirconium Carbide With Iodine

Zirconium carbide was prepared by sintering zirconium oxide* with carbon powder, taken in stoichiometric proportions, and by gradually increasing the heat to 1,900-2,000°C in a vacuum furnace with a graphite heater.

The following over-all reaction took place

$$ZrO_2 + 3\,C = \longrightarrow Zr\,C + 2\,CO$$

which under given conditions shifted entirely to the right. After sintering, the powderlike product was melted in a MIFI-9-3 arc furnace (Moscow Institute of Physical Engineering) in a water-cooled copper crucible, after which operation the zirconium carbide acquired a brilliant metallic gray color.

The remelted product was subjected to chemical and radiographic analysis which confirmed the formation of zirconium monocarbide.

(1) Titan, Izd. I. L., Moscow, (Collection No. 3), 1954.

* Zirconium oxide contained the following impurities: Si - 0.05%, Hf - 0.03%, Fe - 0.04%, Ni - 0.001%, Ti and Mn were not found.

The chemical composition (in percent) of remelted zirconium carbide is given in Table 1.

Table 1

Data	Zr Content %	C Content %
Theoretical	88.43	11.57
Experimental	85	15 (general) 4.5 (free)

Remelted zirconium monocarbide was crushed in a cast iron mortar and screened through 100-150 mesh sieves. Iron particles from the mortar walls were eliminated from the powder magnetically and by leaching with hydrochloric acid. Thereupon, the powder was washed in hot distilled water and dried with alcohol and ether.

Quartz ampoules were used for the study of zirconium carbide obtained in reaction with iodine. The ampoule, into which a certain quantity of carbide was charged, was pumped out to $1 \cdot 10^{-4}$ mm Hg vacuum and was heated to 900-1,000°. After cooling, a certain quantity of iodine was sublimated into the ampoule. Then, that part of the ampoule which contained carbide was gradually heated. Iodine vapors reacted freely with the carbide. The first traces of zirconium iodide were detected at a temperature of 500-520°, however, at this temperature the reaction was very slow. With rising temperature the reaction rate increased fairly rapidly. The graph showing the dependence of the iodine reaction with zirconium carbide on the temperature is shown in Fig. 1.

In all tests the ampoule was charged with 1 g zirconium carbide powder and 0.5 g iodine. The graph shows that the reaction already takes place at an adequate speed at 700-800°C.

The determination of the zirconium tetraiodide yield from the zirconium carbide in reaction with iodine,

$$ZrC + 2I_2 \text{ ----- } ZrI_4 + C,$$

as carried out in the following experiment. In a quartz ampoule 0.5 g zirconium carbide and 2.5 g iodine were char-

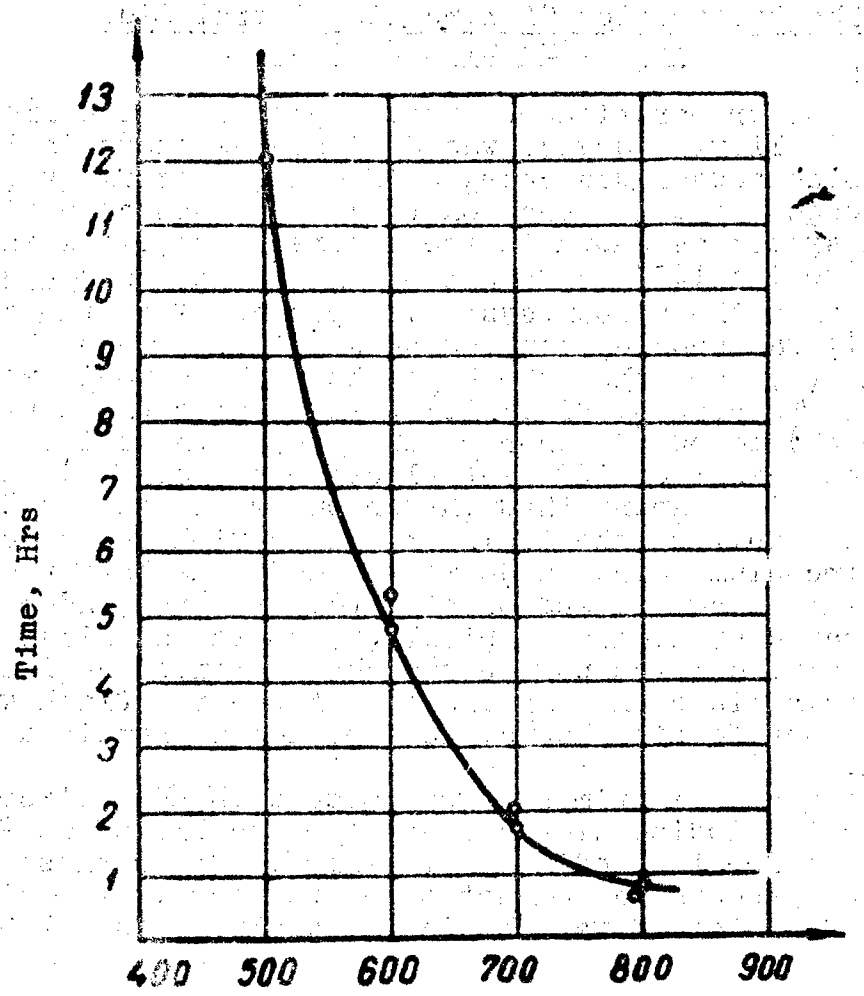

Fig. 1 Dependence of the rate of iodine and zirconium carbide reaction on temperature.

ged; the ampoule was kept at 780 to 800°C for 15 hours. The zirconium carbide residue after leaching of the ZrI_4 was analyzed for zirconium content. The zirconium tetraiodide yield was /found to be/ 97 percent.

The Preparation Of Zirconium Tetraiodide From Zirconium Carbide

For the preparation of zirconium tetraiodide from the carbide the following device was designed as shown in Fig. 2.

Carbide powder was charged into a quartz flask (1) which, through a ground junction (12), was connected with the vacuum system as shown in the figure. The flask was pumped out to $1 \cdot 10^{-4}$ mm Hg under heating to 900°C and welded off from the vacuum system. Upon cooling, the glass ampoule (11) was broken; the iodine sublimated into the quartz tube (9), and the tube with the emply ampoule was welded off. Thereupon, flask (1) with carbide was heated by furnace (3) to 800°C, whereas tube (9) with iodine rose to 80°. The pressure differential between tubes (9) and (6) forced iodine vapors through zirconium carbide powder.

As a result of the iodine reaction with the zirconium carbide, zirconium tetraiodide was formed, the latter concentrated in the cooled end of pipe (6) (the remainder of the pipe was heated by nichrome spiral (5)). In the first tests, 160 g zirconium carbide powder was charged into the flask, and 20 g iodine into the ampoule(1). After the flask was heated for four to five hours, no free iodine remained in the system.

Subsequent experiments were made with 50 g zirconium carbide and 5 g iodine at a carbide temperature of 800° and a temperature for the iodine of 100-110°. Under these conditions, the process lasted not over two hours. The zirconium iodide obtained was chemically analyzed (see Table 2).

(1) Iodine quantity was arbitrary. For full utilization of 160 g carbide, 400 g iodine are required. With low iodine charges, carbide was reused several times.

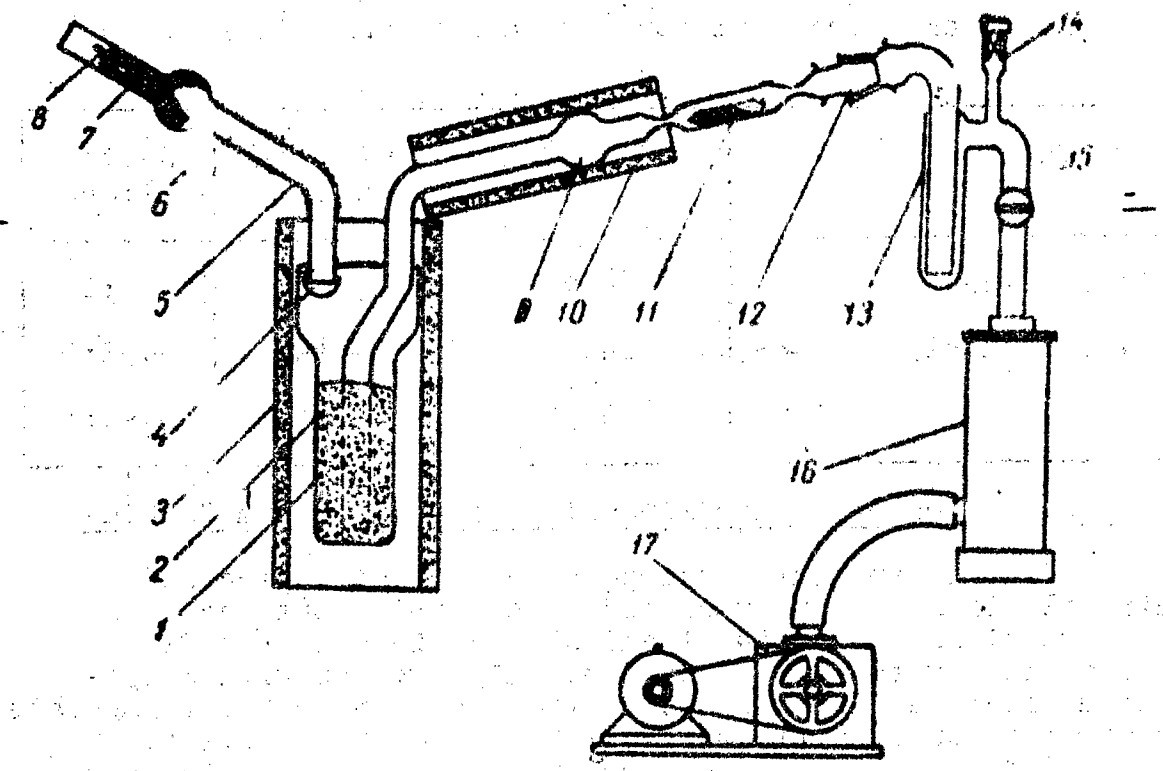

Fig. 2 Schematic /diagram/ of the installation for preparing zirconium tetraiodide from zirconium carbide:

1 - quartz flask; 2 - zirconium carbide; 3 - electric furnace; 4 - quartz cap; 5 - nichrome heater; 6 - quartz collecting tube for ZrI_4; 7 - ZrI_4; 8 - drawn point (to facilitate subsequent distillation of ZrI_4); 9 - quartz tube for iodine supply; 10 - electric furnace; 11 - ampoule with I; 12 - ground junction; 13 - trap; 14 - gauge tube; 15 - valve; 16 - diffusion pump; 17 - prevacuum pump.

Table 2

Iodine and zirconium content in zirconium tetraiodide

Data	I Content (%)	Zr Content (%)	Ratio I:Zr
Theoretical	84.77	15.23	4:1
Experimental	84.41	14.44	3.93:1
"	84.52	15.44	3.94:1

Preparation of Iodide Zirconium from Zirconium Carbide

The experimental preparation of iodide zirconium directly from zirconium carbide was carried out according to directions by Van Arkel and de Bour in a quartz flask 300 mm ling with 35 mm diameter. A glass cap with molybdenum electrodes was welded to the flask through intermediate glass. A tungsten filament, with a diameter of 0.1 mm, was suspended from a tungsten wire by means of porcelain insulators. The flask with the carbide was previously degassed at 900°C. Thereupon, iodine was sublimated into the flask and welded off from the vacuum system. During the experiment the flask was heated to 780-800°, and the cap placed into a separate furnace and heated to 300-400°C.

The filament was heated to 1,300-1,400°C. The growth of the filament was very slow (0.8 mm during four hours), and the filament was black upon cessation of the heating. After the experiment the deposition on the filament was subjected to radiological analysis. The latter showed that the filament consisted of zirconium carbide. No lines of metallic zirconium were identified on the radiogram.

Conclusions

1. Conditions were determined under which iodine reacts with zirconium carbide and forms zirconium tetraiodide with a nearly theoretical yield. The reaction is of practical interest for the preparation of zirconium from zirconium tetraiodide in an electric arc or on hot surfaces.

2. The design of a laboratory device of quartz for the production of zirconium tetraiodide from zirconium

carbide was experimentally tested and verified. This design can be applied on a larger laboratory scale for the verification of the process.

3. It was shown that using zirconium carbide (instead of metallic zirconium) in the usual Van Arkel and de Bour process, a product is deposited on the filament which is essentially zirconium carbide. The mechanics of carbon transfer to the filament was not studied in the present work.

Concerning The Method Of Regeneration of Zirconium And Iodine In The Iodide Refining Process*

/Following is a translation of an article by A. I. Yevstyukhin and A. A. Bakakina in Metallurgiya i Metallovedeniye Chistykh Metallov (Production and Physical Metallurgy of Pure Metals), No. 1, Moscow, 1959, pages 84-90./

Theoretically, iodine is not consumed in the iodide refining of zirconium. If a good method of regeneration were available, all of the iodine could be returned to the process after each refining cycle, except for some mechanical losses during the discharge of the device and for water leaching. In each cycle a certain portion of zirconium iodide prepared is sublimated and deposited on colder parts of the device. Therefore, when the processing is carried out in a glass flask or in metal apparatus, it is expedient to provide a welded ampoule or a collector in the lid of the metal apparatus (Fig. 1), into which the remaining zirconium iodide can be distilled at the end of the process. Subsequently, the ampoule is welded off from the glass apparatus, or the slide gate of the collector in the metal apparatus is closed, and zirconium tetraiodide can be used in a new refining cycle instead of iodine. Nonsublimated zirconium tetraiodide or lower nonvolatile iodides must be leached out before unloading the apparatus, so as to be able to use nonreacted zirconium chips for subsequent refining cycles. To achieve this /desideratum/, the opened apparatus, after removal of the zirconium rod, is usually washed carefully with water. Zirconium iodides (both on the chips and on apparatus walls) are dissolved and collected in the leaching water.

To reduce the cost of iodide refining, a complete extraction of zirconium and iodine from leaching water is required, /a condition/ which is quite possible and practically feasible by employing the method described below.

Essence of the Method

At the moment when the first water portions contact the zirconium iodides during washing of the apparatus, a

(*) In this article a part of the work done by the authors in 1954 is described.

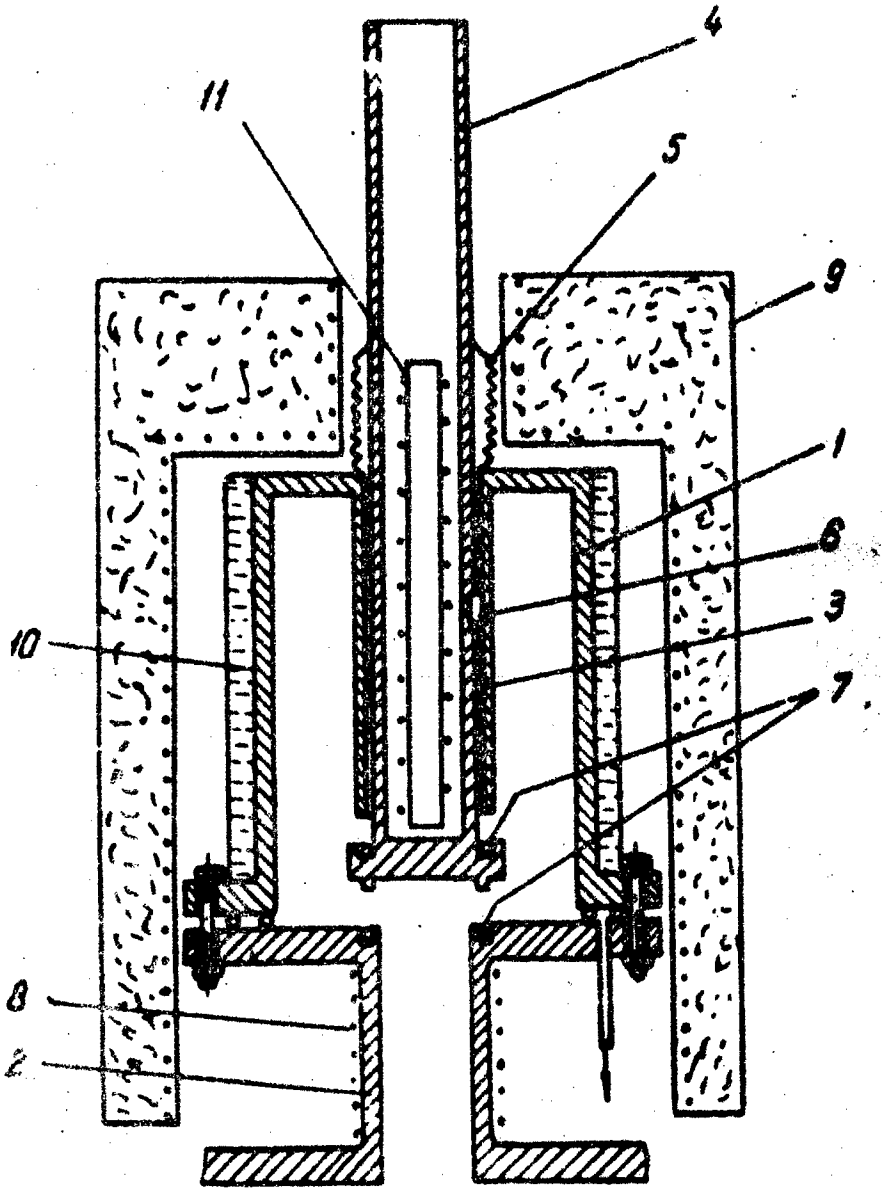

Fig. 1 Schematic diagram of device for the distillation of tetraiodide and for control of its vapor pressure in zirconium refining:

/Legend continued on next page/

/Legend continued from page 29/

1 - collector for distilling zirconium tetraiodide, 2 - tube with flange for hermetic connection of collector (1) with inside space of apparatus, 3 - interior heating cylinder, 4 - closing cylinder with shoulders and grooves for vacuum gaskets, 5 - "sil'fon", 6 - safety device, 7 - vacuum gasket of corrosion resistant soft metal, 8 - heater, 9 - furnace with automatic temperature regulation, 10 - water jacket for cooling, 11 - heater.

light hissing is heard accompanied by elimination of the hydrogen and the formation of hydriodic acid and zirconyl iodide, apparently according to the reactions:

$$ZrI_4 + H_2O \longrightarrow ZrOI_2 + 2HI \qquad (1)$$

$$2ZrI_3 + 2H_2O \longrightarrow 2ZrOI_2 + 2HI + H_2 \qquad (2)$$

$$ZrI_2 + H_2O \longrightarrow ZrOI_2 + H_2 \qquad (3)$$

The composition products of zirconium tetraiodide are easily soluble in water. Low zirconium iodides ZrI_2 and ZrI_3 dissociate while being dissolved, but hydrogen only is eliminated from the solution as a gas, following reactions (2) and (3). In refining tests when the same zirconium chips are reused many times, the leaching water, in addition to the dissolved iodide and the hydriodic acid, contains a suspension of finest zirconium particles with some of its oxide (so-called slurries). This suspension does not settle for many days, cannot be filtered under vacuum, nor centrifuged. Complete washing of the chips is achieved after repeated shaking and decanting of the wash water. Considering the high solubility of zirconyl iodide, a greater concentration of the latter is achieved by repeated use of leaching water in the process, which is of great importance for work on a greater scale.

To eliminate zirconium suspensions from the wash water, the latter can be treated with ammonia or caustic without prior separation of the suspension. In this case, the latter is entrained in the precipitation of zirconium hydroxide, and both can be eliminated by filtration.

After the precipitate is separated from the iodine-containing filtrate, zirconium hydroxide can be calcined to the oxide. The iodine in the leaching water is converted into ammonium and sodium iodides during the precipitation of the hydroxide, as it appears from reactions

$$ZrOI_2 + 2NH_4OH + H_2O \longrightarrow Zr(OH)_4 + 2NH_4I \quad (4)$$

$$HI + NH_4OH \longrightarrow NH_4I + H_2O \quad (5)$$

It is more expedient to carry out the precipitation with caustic soda. If ammonia is used, a crust of ammonium iodide can be formed during evaporation to a small volume, and this salt easily sublimates.

By precipitation with caustics (sodium or potassium) no iodine is lost, but zirconium oxide is contaminated by sodium or potassium.

Iodine regeneration from leaching water containing iodine can be easily achieved by iodine distillation from the acidified medium (sulfuric acid can be used) in conformity with known reductions in the presence of ferric sulfate, potassium bichromate, etc:

$$2NH_4I + Fe_2(SO_4)_3 \rightarrow 2FeSO_4 + (NH_4)_2SO_4 + I_2 \quad (6)$$

liquid liquid liquid liquid solid

Iodine can be also separated by the chlorination of the leaching water

$$2NH_4I + Cl_2 \longrightarrow 2NH_4Cl + I_2 \quad (7)$$

liquid gas liquid solid

If the solution contains caustic, secondary reactions can take place, namely, iodine oxidation and the formation of iodic acid salts

$$3I_2 + 6NH_4OH \longrightarrow 5NH_4I + NH_4IO_3 + 3H_2O \quad (8)$$

solid liquid liquid liquid liquid

Iodine oxidation can also take place in the presence of chlorinated water

$$\underset{\text{solid}}{I_2} + 5\underset{\text{gas}}{Cl_2} + 6\underset{\text{liquid}}{H_2O} \longrightarrow 10\underset{\text{liquid}}{HCl} + 2\underset{\text{liquid}}{HIO_3} \qquad (9)$$

One cannot eliminate iodine completely by wash water chlorination, unless one can eliminate detrimental reactions (8) and (9).

Apparatus

To carry out such reduction under laboratory conditions, the filtrate, after separation of the zirconium hydroxide, is placed in a round-bottomed glass flask or in an enameled reactor, and sulfuric acid is added until a weak acid reaction is achieved, as well as ferric sulfate or ferric ammonium alum in a certain excess of the stoichiometric proportions. Then the flask is heated to boiling, and the sublimated iodine is collected into a condenser which can be a flask with water cooled to 0°. An enameled container can be used as a condenser in actual production.

For the more complete distillation of iodine and for avoidance of clogging of the pipeline from the evaporator to the concenser, the use of a steam generator, as schematically shown in Fig. 2, is recommended.

There are two orifices in the stopper of the evaporating flask. A tube is passed through one of them to the bottom of the flask, and is connected to the steam generator. The outlet tube passes through the other orifice to the condenser. The condenser contains some water, so that the end of this tube is submerged.

Under laboratory conditions, the condenser is cooled with snow or ice to below room temperature (as at room temperature iodine evaporates relatively fast).

Before starting the installation for iodine distillation, the steam generator must be put in action, and only after the steam fills the reactor flask must the same be heated. Crystalline iodine deposited in the condenser is separated from the water and dried with calcium chloride and phosphoric anhydride. Water saturated with iodine can be reused for the collection of the next lost of distilled iodine.

The iodine extraction from the wash water approaches 100 percent, less small mechanical losses.

The rate of iodine distillation is very high -- one cycle of distillation does not exceed 30 to 60

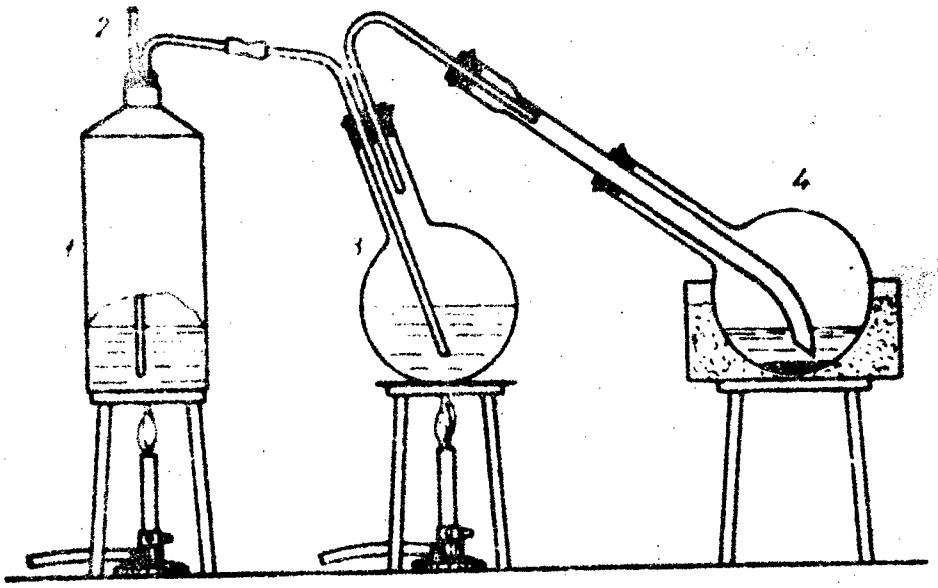

Fig. 2. Schematic diagram of laboratory installation for distillation of iodine vapors from sodium or ammonium iodide solution:

1 - steam generator, 2 - safety tube, 3 - flask with iodide containing solution, 4 - condenser for collection of iodine.

minutes. The complete flow diagram of zirconium and iodine regeneration from the tailings of refining are shown in Figs. 3 and 4.

Conclusions

It was shown experimentally that iodine in the iodide refining of zirconium can be fully recycled, except for small mechanical losses during the unloading of the apparatus and the processing of wash water. The chemical department of the iodide zirconium refining division must possess the following basic equipment:

1) Reactors for washing zirconium chips after their unloading from the apparatus.
2) Filters for the separation of wash water from zirconium chips.
3) Collectors of wash water.

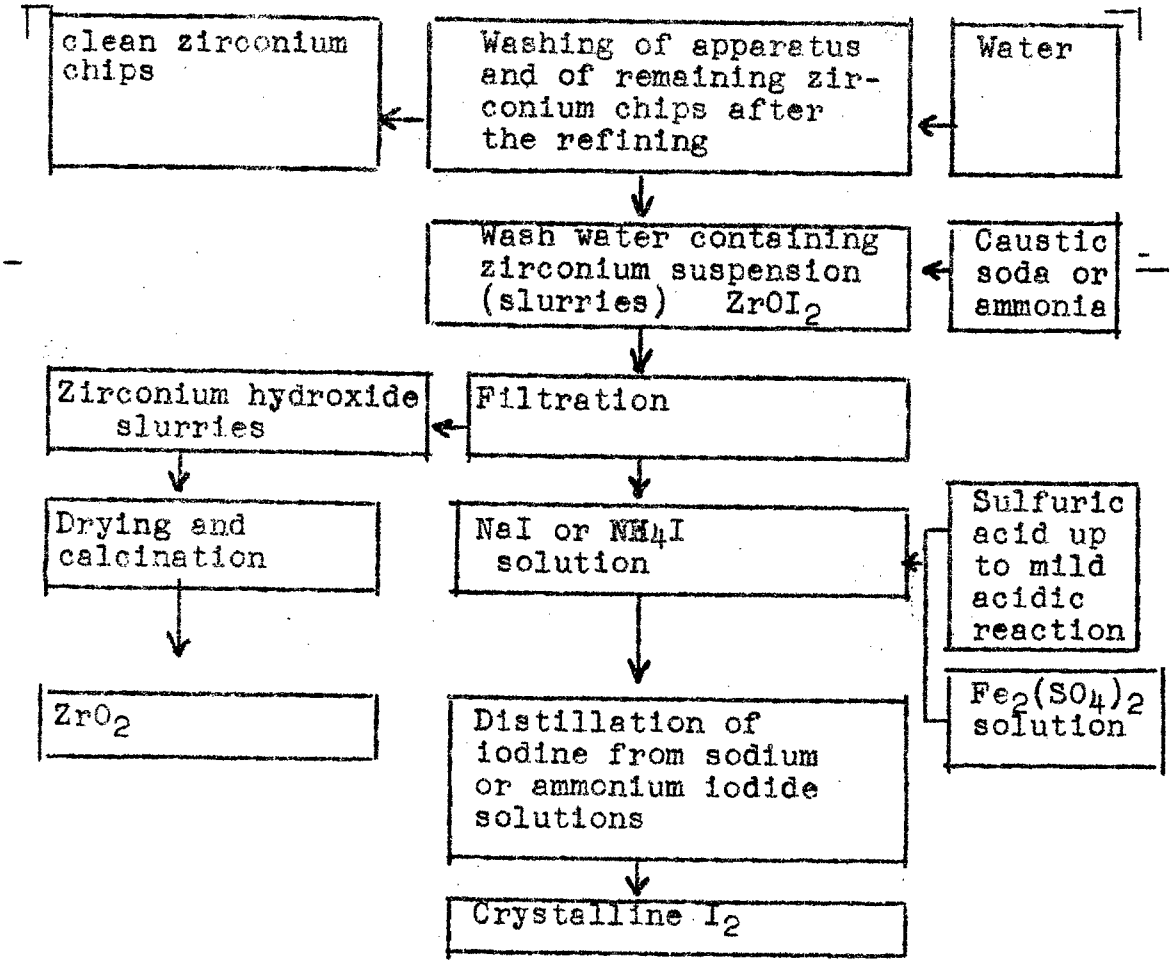

Fig. 3. Flow diagram of zirconium and iodine regeneration from wash water by iodine reduction and distillation.

4) Reactors for the precipitation of zirconium hydroxide from wash water by caustic or ammonia.

5) Filters and centrifuges for the separation and washing of zirconium hydroxide.

6) Apparatus for the decomposition of iodides and for iodine distillation or its elimination by chlorination of the wash water after the elimination of zirconium hydroxide.

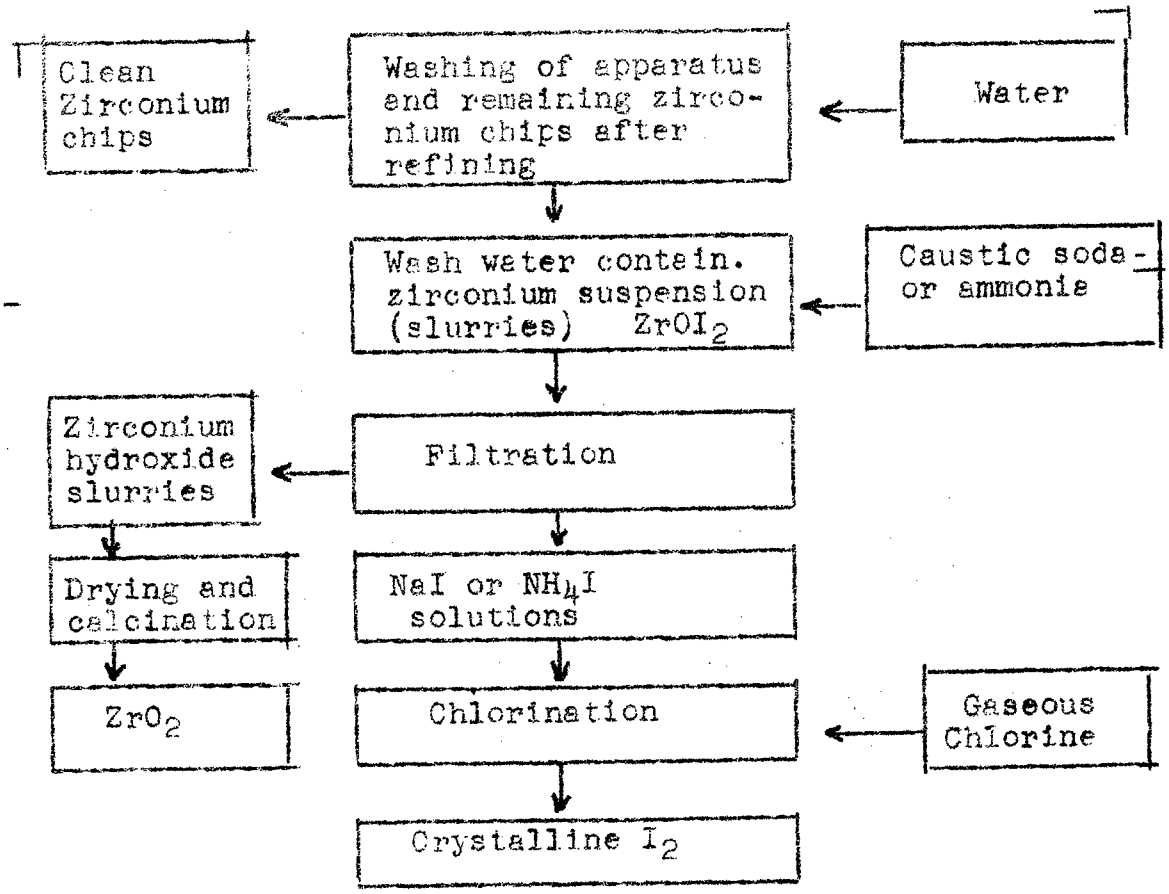

Fig. 4. Flow disgram of zirconium and iodine regeneration from wash water by chlorination.

7) Furnaces for the calcination of zirconium hydroxide and drying chambers for regenerated zirconium chips.

8) Apparatus for iodine sublimation and for its refining and recycling into the zirconium refining process.

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