62-134

**287 702**

METALLURGY, METALLOGRAPHY, AND PHYSICAL-CHEMICAL
INVESTIGATION METHODS

(SELECTED ARTICLES)

# UNEDITED ROUGH DRAFT TRANSLATION

# TABLE OF CONTENTS

# A PHASE EQUILIBRIUM DIAGRAM FOR THE
# TITANIUM-VANADIUM-IRON SYSTEM

By Bi Tsin-Khua and I.I. Kornilov

References [1-3] contain information on the general problems
of the reactions of titanium with other elements depending on the
position of the combinatory elements in the Mendeleyev periodic
system and on the basic types of phase diagrams for binary systems
based on titanium.

The phase diagram of the Ti-V system [4-5] is related to a
system containing saturated solutions of $\beta$-titanium and unsaturated
solid solutions of $\alpha$-titanium. The Ti-Fe phase diagram [6-9] is
related to the system which contains unsaturated solid solutions
of $\alpha$- and $\beta$-titanium.

As yet, no results have been published for research on the
phase diagram of the ternary titanium-vanadium-iron system before
the formation of $TiFe_2$. Just recently, the authors of this article
studied the two quasibinary sections of this system, TiFe-V and
$TiFe_2$-V, and constructed their phase diagrams [10, 11], which served
as the basis for studying the ternary system.

The object of this article is to study the phase diagrams of
the portion of the ternary titanium-vanadium-iron system bounded
by the vertices of the Ti and V concentration triangle, before the
formation of TiFe.

The quasibinary section TiFe-V is the basis for the formation

- 1 -

of the secondary system Ti-TiFe-V [10].

This research was carried out by microstructural and X-ray analysis. The compositions of the alloys were studied along radial cross sections in specimens with titanium-iron ratios of 95:5, 90:10, 84:16, 80:20, 70:30, and 60:40.
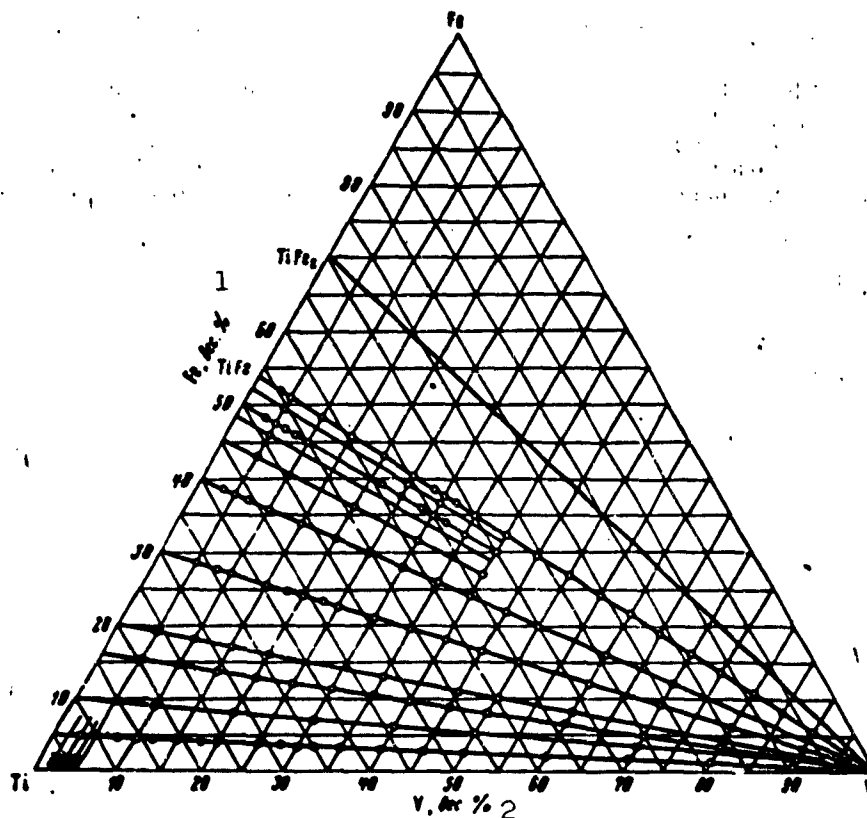


Fig. 1. Location of alloys studied, on the concentration triangle. 1) Fe, % by weight; 2) V, % by weight.

The initial materials for producing the majority of alloys were metallic vanadium (98.7% pure V), TiFe premelted in an arc furnace (45.94% Ti by chemical analysis), and TG-0 sponge titanium (99.67% Ti), while a number of the specimens were made from titanium produced by the iodide method (99.79% pure Ti) in order to determine precisely the boundary of the titanium-based α-solid solution.

The alloys were smelted in an arc furnace in an argon atmosphere, the air first being evacuated.

The alloys obtained were subjected to prolonged annealing, with the following soaking times: at $1000^\circ$ for 48 hours; at $800^\circ$, 100 hours; at $600^\circ$, 200 hours; and at $550^\circ$, 100 hours. The specimens were then cooled together with the furnace.

Sections of the alloys were pickled in hydrofluoric acid. The results of research on the microstructure of alloys annealed for long periods of time showed that, at room temperature, the following phases existed in the system: 1) four solid solutions, $\alpha$, $\beta$, $\delta$, and $\gamma$, based, respectively, on titanium and vanadium and the compounds TiFe and (TiFe)V; 2) five binary regions, $\alpha + \beta$, $\beta + \gamma$, $\gamma + \delta$, $\alpha + \gamma$, and $\alpha + \delta$; 3) two ternary regions, $\alpha + \beta + \gamma$ and $\alpha + \gamma + \delta$ (Fig. 2).

Data obtained from microstructural studies have shown that the $\alpha_3$-solid solution occupies a very narrow region adjoining the Ti-V side. It is bounded by a vanadium concentration of 4.0 and an iron concentration of 0.5%. On the other hand, the $\beta$-solid solution encompasses a wider region adjoining the high-vanadium side of the Ti-V concentration triangle. As regards the remaining two $\gamma$- and $\delta$-solid solutions, they occupy small areas; the $\gamma$-solid solution region based on the compound (TiFe)V is larger than the $\delta$-solid solution region based on the compound TiFe.

An equilibrium mixture of two phases lies between the single-phase regions. This two-phase area is formed either in crystallization or as a result of various solid-state reactions. The two-phase $\alpha + \delta$ region is formed by a eutectoid reaction in the Ti-Fe system. In the ternary system, it extends along the TiFe side. In the quasibinary TiFe-V system, a two-phase $\gamma + \delta$ region is formed by a eutectic reaction and a $\beta + \gamma$ region is formed by a peritectic reaction. The first region is narrow, but the second is rather wide.

- 3 -

In the Ti-V system, a α-solid solution is formed from the β-solid solution at small vanadium concentrations; beyond this region, there is a two-phase α + β region. In addition, in the central section of the system studied, the three-phase regions α + β + γ and α + γ + δ are observed, separated from each other by the two-phase region α + γ.
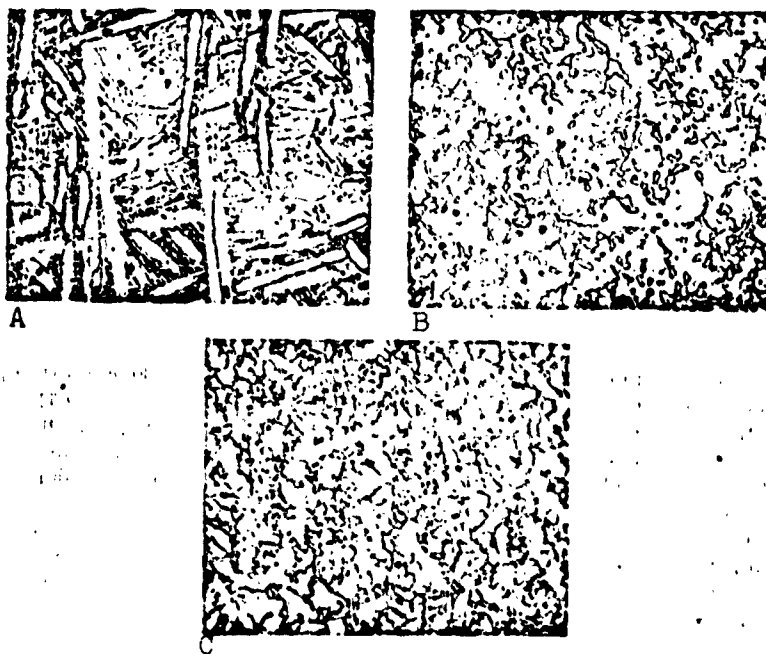


Fig. 2. Microstructure of alloys in system at room temperature (200X). ) 2.0% V + 3.4% Fe, α + δ-phases. b) 50% V + 20% Fe, β + γ-phases; c) 10% V + 36% Fe, α + γ + δ-phases.

The presence of these two three-phase regions has been confirmed by X-ray analysis. However, it should be pointed out that vanadium and the compound TiFe have identical body-centered cubic crystal lattices with nearly the same constants (a = 3.0338 Å for vanadium, a = 2.97 Å for TiFe) [12]. Consequently, it is difficult to determine the boundaries of the ternary regions α + β + γ and α + γ + δ from X-ray data. These boundaries are more precisely determined by microstructural analysis. Figure 3 shows the results of the study of the phase equilibrium of the secondary ternary system

- 4 -
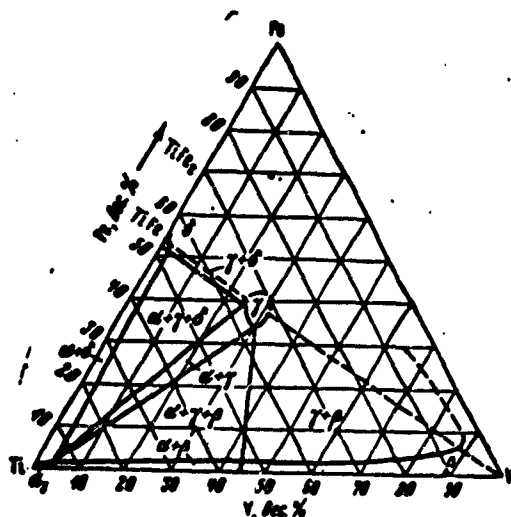
Fig. 3. Phase equilibrium dia-
gram of system at room tempera-
ture. 1) Fe, % by weight;
2) V, % by weight.
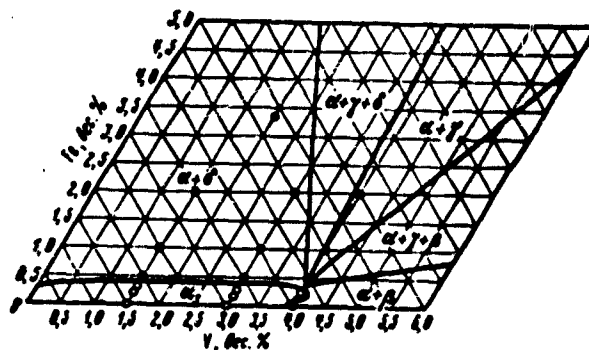
Fig. 4. $\alpha_3$-phase region in Ti-
V-Fe system. 1) Fe, % by weight;
2) V, % by weight.

Ti-TiFe-V, while Fig. 4 shows the $\alpha_3$-solid solution region.

## CONCLUSIONS

Experimental research on the secondary Ti-TiFe-V system by microstructural and X-ray analysis has shown the following.

1. There are four single-phase regions ($\alpha$, $\beta$, $\delta$, and $\gamma$), five two-phase regions ($\alpha + \beta$, $\beta + \gamma$, $\gamma + \delta$, $\alpha + \gamma$, and $\alpha + \delta$), and two three-phase regions ($\alpha + \beta + \gamma$ and $\alpha + \gamma + \delta$).

2. Boundaries exist for the titanium-based $\alpha_3$-solid solution and the vanadium-based $\beta$-solid solution.

3. The other single-, two-, and three-phase regions of the system are bounded.

4. The phases in the studied system are shown in the form of a phase-equilibrium diagram for the ternary system Ti-TiFe-V.

## REFERENCES

1. I.I. Kornilov, Dokl. AN SSSR [Proceedings of the Academy of Sciences USSR], 1953, 41, No. 3, p. 549.

2. I.I. Kornilov, P.B. Budberg, Usp. khim. [Progress in Chemistry], 1956, 25, No. 12.

3. I.I. Kornilov, Zh. neorganich. khim. [Journal of Inorganic Chemistry], 1958, 3, Issue 3, p. 571.

4. H.K. Andenstedt, J.R. Pequignot, J.M. Raymer. Trans. ASM, 1950, 44, 990.

5. P. Pietrokcwsky, P. Duwez. Trans. Am. Inst. Min. Metall. Eng., 1952, 194, 627.

6. P. Duwez, J.L. Taylor. Trans. Am. Inst. Min. Metall. Eng., 1950, 188, 1197.

7. H.W. Worner, J. Inst. Metals, 1951, 79, 73.

8. R.J. Van-Thyne, H.D. Kessler, M. Hansen. Trans. ASM, 1950. 44, 974.

9. I.I. Kornilov, N.G. Boriskina. Dokl. AN SSSR, 1956, 108, No. 6.

10. Bi Tsin-khua, I.I. Kornilov, Zh. neorganich. khim., 1960, 5, Issue 4, p. 902.

11. Bi Tsin-khua, I.I. Kornilov. Izv. AN SSSR, OKhN [Bulletin of the Academy of Sciences USSR, Department of Chemical Sciences], 1959, No. 6.

12. G.B. Bokiy. Vvedeniye v kristallokhimiyu [Introduction to Crystal Chemistry], Izd. Mosk. gos. un-ta [Moscow State University Press], 1954.

# VANADIUM AND THE AREAS OF ITS APPLICATION

## By N.I. Kornilov and N.M. Matveyeva

Vanadium is an element in Group V of Mendeleyev's periodic
system of the elements. It was discovered at the beginning of the
19th century, in an era of rapid and fruitful progress in chemical
science. The history of the development of vanadium is elucidated
in works [1-3].

Vanadium was first detected in 1801, but for a long time was
mistaken for chromium. Credit for the definite discovery of vanadium
belongs to the Scandanavian chemist Sefstrom who, in 1830, detected
it in Swedish iron ore. Sefstrom studied vanadium compounds and
named the newly discovered element. In Russia, vanadium was found
in 1834 in the Berezovskiy mine near Yekaterinburg. Brown prismatic
crystals of a new mineral resembling vanadinite, according to the
description given by Rose, were found in the green lead ore from
this mine. Later, "at the end of 1838, a new mineral was observed
in the mines belonging to the Perm State Plants. This mineral ac-
companied ore-bearing sandstone as an incrustation or in the form
of thin sheets gathered into a kidney-like shape. The thin, soft
sheets of this mineral were citron yellow in color and had a pearly
luster." According to studies by Shubin, the newly discovered
mineral was copper vanadate — the mineral volborthite — of which
no deposits were then known [5]. A large contribution to the crea-
tion of a chemistry of vanadium was made by the work of Veller,

Berzelius, and Roscoe and especially by that of Roscoe who, in 1867 first obtained vanadium in the metallic state by reducing vanadium dichloride with hydrogen. Roscoe pointed out the chief properties of vanadium, synthesized and studied its compounds, and corrected certain erroneous ideas about vanadium compounds which had been established before the element was obtained in the free state.

In particular, supplementing Berzelius' research on vanadium, he showed that the substance which Berzelius assumed to be pure vanadium was actually a mixture of vanadium compounds, of vanadium nitride and vanadium dioxide. Finding that vanadium and phosphorus had analogous properties, Roscoe incorporated them in one group.

Roscoe's research on vanadium was highly regarded by D.I. Mendeleyev [6]. In 1871, when his periodic law and periodic table were published, D.I. Mendeleyev had already placed vanadium in Group V, subgroup VA, together with niobium and tantalum. Since that time, vanadium has justly occupied this position, in accordance with its chemical properties and physical parameters, despite the attempt made in the 20th year of this century [2] to equate vanadium with arsenic, antimony, and bismuth.

## The Occurrence of Vanadium in Nature.

Among the metals of practical importance, vanadium occupies seventh place, following chromium, so far as occurrence in nature is concerned [7]. The extent of its occurrence is the same as that of nickel, zinc, and zirconium, as shown below (by weight, %).

| V | Nb | Ta | Cr | Mo | W | Ti | Zr | Hf |
|---|---|---|---|---|---|---|---|---|
| 0,02 | $3,2 \cdot 10^{-4}$ | $2,4 \cdot 10^{-4}$ | 0,03 | $1 \cdot 10^{-3}$ | $7 \cdot 10^{-4}$ | 0,61 | 0,025 | $4 \cdot 10^{-4}$ |

The data of various authors on the occurrence of vanadium in nature are contradictory. According to the data of V.I. Vernadskiy (1914), the content of vanadium in the crust of the earth is 0.04% by weight and 0.01% in the lithosphere [8]. According to Washington's data (1924) [7], the lithosphere contains 0.021% vanadium by weight. The latter figure, however, fails to account for the elements contained in sedimentary rocks. Certain authors use the A.P. Vinogradov data (1950), according to which the vanadium content in the lithosphere is 0.015% by weight.

With respect to its occurrence in nature, vanadium considerably surpasses its direct analogues niobium and tantalum, as well as molybdenum and tungsten. As may be seen from the data given above, the vanadium in the crust of the earth exceeds the niobium by a factor of 1000 and the tantalum by a factor of 1500. There is considerably more vanadium in the crust of the earth than there is copper, tin, or lead, but these (in contrast to vanadium) are not considered rare elements.

A.Ye. Fersman related vanadium to the group of rare elements because of the peculiarities of its chemical properties. Despite its comparatively wide occurrence, vanadium rarely forms separate minerals and is an extremely dispersed element. Its widest occurrence in nature is in conjunction with iron and titanium, uranium, lead, and copper.

Individual deposits of vanadium are associated with sedimentary rocks (sandstones, asphalts, coal, and bitumen).

There are 65 minerals which contain vanadium, but only a few are of industrial importance. The compositions, structures, derivation, and deposits of minerals containing vanadium are described in works [1, 7, 9-11].

Groups of minerals containing a substantial quantity of vanadium were also cited. In addition, the list includes certain less important natural chemical compounds of vanadium which can serve as an additional source of vanadium when ore containing the basic minerals is subjected to complex processing.

Patronite — $VS_2$
Sulvanite — $Cu_3VS_4$
Kolyuzite — $CU_3(As, Sn, V)S_4$
Titanomagnetite (containing) — $(Fe, Ti)_3O_4$
Minasragrite — $V_2O_4SO_4 \cdot 16H_2O$
Pucherite — $BiVO_4$
Vanadinite — $Pb_5[VO_4]_3Cl$
Descloizite — $(Zn, Cu) Pb [VO_4] [OH]$

Volborthite — $CuCa [VO_4] [OH]$
Brackebuschite — $Pb_2(Mn, Fe)[VO_4]_2H_2O$
Pyrobelonite — $MnPb[VO_4] [OH]$
Turanite — $Cu_4[VO_4] [OH]_5$
Uzbekite — $CU_3[VO_4] \cdot 3H_2O$
Tjuiamunite — $Ca[UO_2]_2[VO_4] \cdot 8H_2O$

Carnotite — $K_2[UO_2]_2[VO_4]_2 \cdot 3H_2O$

Fervanite — $Fe[VO_4] \cdot 2H_2O$
Rossite — $CaV_2O_6 \cdot 4H_2O$
Metarossite — $CaV_2O_6 \cdot 2H_2O$
Korvusite — $V V_2O_{17} \cdot UH_2O$
Roscoelite — $KV_2[AlSi_3O_{10}] [OH]_2$

The principal minerals which are sources of vanadium are underlined. Some of them are very rare. For example, partonite, the mineral richest in vanadium (52% $V_2O_5$ after roasting), is found in a single large deposit in the Peruvian Andes. Roscoelite is a very rare potassium-vanadium mica and is found in the United States (in the states of California and Colorado) and in Western Australia. The vanadium-containing titanomagnetites, vanadinites, and carnotites occur more widely.

Titanomagnetites contain vanadium oxide in quantities of several tenths of a percent. Thanks to the wide occurrence of these types of ore in the USSR and China, they are the principal source of vanadium in these nations.

There is an industrial enterprise in Otanmek in Finland which processes 180,000 tons per year of titanium-ilmenite ores containing 0.58% vanadium after mechanical concentration. The final product contains 90% $V_2O_5$ and is exported to Sweden for the production of ferrovanadium.

Not counting low-content ores, the total supply of vanadium in the capitalist nations before the second World War was estimated at approximately 43,000 tons; of this quantity, 32,000 tons were in Peru, 7,000 tons in the United States, 3,000 tons in South West Africa and 1,000 tons in Mexico.

During recent years, new deposits of vanadium ores have been discovered in the United States, Sweden, Argentina, and Rhodesia [12]. The United States produces more than 50% of the world's vanadium. According to the statistical data known at the present time, the consumption of vanadium in the United States during the period from January to September 1956 was 1316 tons.

South West Africa is a large-scale producer of vanadium, producing 907 tons of $V_2O_5$ in 1956. The imports of vanadium concentrate to Great Britain during 1956 were estimated at 272 tons and this is currently on the rise as a result of the use of vanadium in atomic reactors [13].

According to recent data [14], 7000 tons of $V_2O_5$ are mined in the world each year and this can be considerably increased.

### Methods of Extracting Metallic Vanadium

Metallic vanadium is regarded as an element which is very dif-

ficult to obtain in pure form. It is easily oxidized at high temperatures and, because of its high reactivity, produces stable, high-melting compounds with metalloids.

The plastic properties of pure metallic vanadium vary sharply when its oxygen content exceeds 0.05% and its nitrogen content exceeds 0.03% [15-18]. Consequently, the degree of purity of vanadium is measured in terms of its adaptability to various forms of mechanical processing, since considerable quantities of oxygen, nitrogen, or hydrogen will make it brittle and hard.

It is noted in the literature that there is not a single metal which is as difficult to obtain in pure form as vanadium [19]. The methods which had already been worked out in the 19th century for obtaining metallic vanadium by reducing its pentoxide with silicon, carbon, hydrogen, or aluminum made it possible to obtain technically pure vanadium containing up to 5% impurities.

Moissan, Goldschmidt, Weiss, Ruf [sic], and others attempted to obtain pure vanadium either by the aluminothermal method or by electrothermal reduction with hydrogen. As a rule, the metallic product obtained contained fewer vanadium oxides or reducing-agent impurities. However, the aluminothermal methods have remained of very great importance to the present day for the extraction of vanadium from ores and for the production of ferrovanadium.

In 1923, Hunter and Jones [2] obtained vanadium powder which was, in the opinion of the authors, 99.5-100% pure by reducing $VCl_3$ with sodium in a steel bomb; the metal produced by this method was in powder form. The authors gave no description of the properties of the metal obtained, since they did not have the dense metal on which to determine these properties.

In 1927, Marden and Rich [20] used metallic potassium for the

first time for the purpose of reducing vanadium pentoxide. The reaction $5Ca + V_2O_5 = 5CaO + 2V$ was carried out in the presence of calcium chloride in an evacuated steel bomb at a temperature of 900-950° for a period of one hour. As a result of this reaction, we obtained an ingot of soft, ductile metal containing 99.8% vanadium.

Research on methods of obtaining pure vanadium was carried on by many authors [18, 23, 26-29].

All existing methods for obtaining pure plastic vanadium may be expediently divided into methods involving the reduction of vanadium compounds and methods involving the refining of crude, technically pure vanadium. This first group of methods can in turn be divided into the reduction of oxides and the reduction of chlorides and oxychlorides.

Methods for refining technically pure vanadium have been worked out and employed in recent years; among these we should note the thermal decomposition of vanadium diiodide, $VI_2$, the electrolytic precipitation of vanadium, and the vacuum and zone melting of vanadium by electron bombardment.

At the present time, the chief method for obtaining metallic vanadium is the calcium-thermal method of reducing vanadium pentoxide, which was considerably modified at the time of work [20] and serves as the basis for the industrial production of vanadium.

Work [21] notes the advantages of the use of the calcium-thermal method for reducing oxides over its use for reducing chlorides and oxychlorides and examines in detail the special features of the method of reducing vanadium oxides with calcium.

These special features consist, first of all, in the correct selection of the flux for diluting the slag; secondly, they consist in the addition of substances which increase the temperature of the

charge to the reaction temperature by liberating heat in their reaction with calcium, and thirdly, in the correct choice of the charge composition so that reaction occurs and the optimum yield of metallic product is obtained.

Gregory [22] used vanadium trioxide rather than vanadium pentoxide as the original product, a considerably smaller quantity of expensive calcium being required to reduce the former. Gregory's method consisted in the following: 1) $V_2O_5$ is reduced to $V_2O_3$ by hydrogen at a temperature of $600^\circ$ in a tubular furnace; 2) the brownblack reaction product is pulverized and mixed with finely divided metallic calcium and powdered calcium chloride in proportions of 1 mole $V_2O_3$, 6 moles Ca, and 1 mole $CaCl_2$.

The calcium chloride is added to the charge as a flux to melt the calcium oxide and to eliminate the high-melting film which this compound forms on the surface of the reactive substances. Calcium oxide contributes to the formation of larger grains in the reduced metal. When the ratio of $CaCl_2$ to $V_2O_3$ equals 1:1, the reaction temperature ($1900^\circ$) reaches a value approximating the calculated value.

An excess of 100% calcium over the amount theoretically required gives better results so far as the purity and plasticity of the vanadium obtained are concerned. Figure 1 shows the apparatus in which the reduction of vanadium trioxide takes place in a vacuum device. The reaction mixture 1 is placed in crucible 2 mounted on an insulated support 3 within an iron container 4 which is connected to the vacuum system 5, evacuated to 100 μ, and filled with pure argon. The pressure under which the argon is supplied to the reaction vessel is controlled by a manometer and is 0.8 atm. The crucible and container are lined with magnesium and calcium oxide

to prevent fouling by iron. The charge is heated in a high-frequency furnace to the temperature at which the reaction begins and is then kept at 1000° for one hour. The mass remaining after the reaction has been completed is washed with 40-50% acetic acid and the vanadium powder is then washed out of the acetic acid with water by decantation, filtered, and vacuum dried at a temperature of 40-50°.

The chemical composition of the impure vanadium obtained by the method described is shown in Table 1.

TABLE 1

Chemical Composition of Impure Vanadium, %.

| Литературный источник [1] | O | N | H | C | Fe | Si | Ca | Прочие [2] |
|---|---|---|---|---|---|---|---|---|
| Mckechnie [18] | 0,031 | 0,016 | 0,005 | 0,21 | 0,01 | 0,04 | 0,023 | |
| Kinzel [25] | 0,05— | 0,02— | 0,0001— | 0,03— | — | — | — | |
| | 0,12 | 0,04 | 0,004 | 0,07 | — | — | — | |
| Gregory [22] | 0,1— | 0,01— | — | 0,05 | 0,01 | — | 0,05 | |
| | 0,25 | 0,015 | | | | | | |
| Beard a. Crooks [24] | 0,028 | 0,05 | 0,001 | 0,126 | 0,65 | 0,005 | 0,01 | |
| | 0,033 | 0,013 | 0,002 | 0,102 | 0,4 | 0,04 | 0,1 | |
| Nash [19] | 0.012 | 0,006 | 0,005 | 0,005 Al | 0,07 | 0,002 | 0,002Cr | 0,005Mo |
| [3] А. М. Самарин, А. Ю. Поляков и др. [28] | 0,045 | 0,020 | — | 0,20 | — | — | — | |
| | 0,01 | 0,005 | 0,005 | 0,05 | 0,01 | 0,04 | 0,001 | 0,01Al |
| Joly [21] | 0,025 | 0,015 | — | 0,1 | 0,03 | 0,08 | — | 0,03Al |

1) Literature source; 2) others; 3) A.M. Samarin, A.Yu. Polyakov, et. al. [28].

Although Gregory's method makes it possible to obtain cast vanadium, it is also used for the production of powdered metal and of metalloceramic products. In order to use the metallic vanadium powder obtained, it is necessary to convert it to a dense metal. In order to accomplish this, the powder is pressed in steel dies under a pressure of 2.5-3 t/cm$^2$ and is sintered in vacuum furnaces at a temperature of 1400-1500° for 1-2 hours. A vacuum sinter furnace (Fig. 2) consists of a basic cylinder 1 which rests on a copper plate 2 cooled by water. The cylinder and plate are hermetically

joined. Tube 3 serves to remove water from the reaction area. The pressed briquette 4 is suspended in the center of molybdenum tube 5, which rests on the molybdenum block 6 and is held in this position by a molybdenum framework. Tube 5 is enclosed by two shield-screens 7 which reduce heat losses. Heating is effected by induction furnace 8. Vanadium sintered under these conditions is a plastic metal capable of being rolled into sheets, rods, wires, etc. Mechanical processing of hot vanadium is carried out either in an argon atmosphere or in protective steel jackets in a normal atmosphere. The production technology for vanadium products is similar to production technology for titanium, zirconium, and other metals which are easily oxidized on heating.

The production of vanadium products by powder metallurgy is widely practiced in England, where this method is used for the fabrication of vanadium tubes for atomic reactors. In the United States, the smelting of vanadium in vacuum-arc furnaces with expendable electrodes is preferred. This method is used in conjunction with casting in a water-cooled ingot mold, after which the metal is subjected to pressure heat-treatment for the fabrication of products. McKechnie and Seybolt developed a process for the calcium-thermal reduction of vanadium pentoxide in the presence of $I_2$ instead of $CaCl_2$ [18]. Iodine is combined with calcium at a temperature of $425^o$ with the formation of $CaI_2$ and a heat liberation of 100 kcal/mole which initiate the main reaction of the reduction of vanadium trioxide. The change in slag composition where $CaI_2$ is used makes it possible to agglomerate the metal in the form of a hard regulus.

The reaction takes place in a closed magnesite crucible which is inserted in a steel bomb. The bomb is hermetically sealed on top by a copper-lined steel cover. The bomb contains 300 grams of

Fig. 1. Vacuum device for the reduction of vanadium trioxide.

Fig. 2. Vacuum furnace for sintering powdered vanadium specimens.

$V_2O_5$, 552 grams of Ca (60% more calcium than the amount theoretically required) and 150 grams of $I_2$ (0.2 moles of iodine for every 2 moles of vanadium).

The actual yield is 125 grams of varadium or 74% of the theoretical yield. The composition of the vanadium obtained by McKechnie and Seybolt is shown in Table 1. As these authors stated, vanadium has become a metal of great industrial potential rather than a laboratory curiosity as a result of the semi-industrial method which they worked out.

Beard and Crooks showed [24] how to increase the actual yield of metallic vanadium in its production by the method described by McKechnie and Seybolt. These authors increased the actual yield of vanadium from 74 to 84% of the theoretical yield by a wiser choice of charge composition. A conical magnesite crucible with a cover 450 mm high and a diameter of 120 mm across the top was placed in a steel container. Coarse-grained magnesium was used to fill the space between the crucible and the bomb in order to center and support the crucible. The reaction took place in an argon atmosphere.

The charge size varied in accordance with the type of final product; for a powdered product, 2180 grams of $V_2O_5$, 3840 grams of Ca, and 1090 grams of $I_2$ were used; for a cast product, 1635 grams of $V_2O_5$, 2880 grams of Ca, and 818 grams of $I_2$ were used.

Induction heating at a rate of $50-60^\circ$/min was continued until a rapid rise in temperature began due to the reduction reaction. The reaction yielded 770-1020 grams of monocast ductile metal suitable for further mechanical processing. Its composition is shown in Table 1.

The authors also studied the influence of impurities on the plasticity and hardness of the metal. An oxygen content of more than 0.05% or a silicon content of more than 0.2% increases the hardness of the vanadium and makes it unsuitable for mechanical processing. The mean Vickers hardness for plastic metal reguli is 135.

There is basically no difference between the method described and the method developed by McKechnie and Seybolt but there is a characteristic tendency in this type of work to make vanadium a commercially available metal and to present the possibility of a wide use of vanadium and its alloys in modern engineering.

Kinzel [25] reports that the research laboratories of the Electro Metallurgical Co. and the Union Carbide and Carbon Company were able to produce 40 kg of dense metal by this method. The metal had the following composition (%):

$$\frac{V}{99.8-99.9} : \frac{C}{0.03-0.07} : \frac{O}{0.05-0.12} : \frac{N}{0.02-0.04} : \frac{H}{0.001-0.0004} .$$

The Vanadium Corporation of America produces ductile metal. The metal produced by this firm by McKechnie's method has the following composition (%):

$$\frac{V}{98.7} : \frac{C}{0.10} : \frac{Fe}{0.10} : \frac{Si}{0.05} : \frac{Ni}{0.005} : \frac{Cu}{0.01} .$$

Wilhelm and Long [26] and later Joly [21] added comparatively cheap sulfur to the charge rather than calcium chloride or iodine. This made it possible to use technically pure pentoxide, one-seventh as expensive as chemically pure pentoxide, as the original product.

The CaO·CaS formed during the reaction dissolved the impurities in the technically pure pentoxide so that they did not enter the reduced metal.

Calcium chloride in a quantity of 30% more than the amount theoretically necessary was used as a flux in the charge in the experiments described in work [21]. There was a 70% excess of metallic calcium over the amount theoretically required and this ensured a maximum yield of metallic vanadium, 85% of theoretical. The chemical composition of the vanadium obtained by Joly is shown in Table 1; its Vickers hardness was 90.

Several years ago, plastic vanadium was produced at a cost of several hundred dollars per pound. On 1 April 1958, the cost of vanadium containing no less than 99.5% V and produced by the calcium-thermal method was 18.2 dollars per kg [27].

The basic shortcoming of the calcium-thermal method of extracting vanadium is the necessity for consuming large quantities of high-purity calcium, since impurities present in the calcium pass into the vanadium, reducing its plasticity (when calcium containing more than 0.05% nitrogen is used, the vanadium becomes brittle).

According to the data of the Soviet researchers A.M. Samarin and A.Yu. Polyakov, and others [28, 29], the use of carbon as a reducing agent in vanadium production has extremely good prospects. Carbon is a stronger reducing agent than calcium at a reduced gas-phase pressure. Carbon has a lesser tendency to reduce plasticity

than does the oxygen which can be present in quantities of more than 0.1% in vanadium produced by the calcium-thermal method. In the experiments described in work [27], vanadium trioxide obtained by the reduction of chemically pure pentoxide by hydrogen in a tubular furnace at a temperature of $500\text{-}600^\circ$ was used. Lamp black was added as a reducing agent in a quantity 5-7% greater than that stoichiometrically calculated. Briquettes pressed from the reaction mixture were first subjected to preliminary reduction for two hours under a quartz hood at a temperature of $900\text{-}1000^\circ$. The briquettes were heated by a high-frequency inductor placed around the quartz hood. After repeated pulverization and pressing, the briquettes were then subjected to high-temperature reduction in vacuum furnaces evacuated to $1 \cdot 10^{-4}$ mm Hg.

The rate at which vanadium trioxide is reduced depends on the the temperature and degree of evacuation. The reaction rate increases rapidly in the temperature interval $1300\text{-}1125^\circ$ at a pressure of $1 \cdot 10^{-4}$ mm Hg (Figs. 3 and 4).

Fig. 3. Rate of reduction of vanadium trioxide (V%) by carbon in a vacuum ($\sim 1 \cdot 10^{-2}$ mm Hg) at various temperatures. Reducing agent — lamp black. 1) Min.

Fig. 4. Rate of reduction of vanadium trioxide at $1450^\circ$ as a function of degree of evacuation. Reducing agent — lamp black. 1) $1 \cdot 10^{-2}$ mm Hg; 2) 4 mm Hg; 3) 17 mm Hg; 4) without evacuation of CO; 5) min.

The composition of the plastic metal obtained under these con-

ditions is shown in Table 1. The authors of this article established the relationship between the carbon and oxygen contents. As may be seen from Fig. 5, a low oxygen content in the metal (less than 0.10%) is reached only when the carbon content is no less than 0.1-0.25%. With this carbon content, the metal still remains plastic at room temperature.

In the method described, there is a virtually complete conversion of vanadium from oxide to metal and this, together with other factors, is a very important advantage of this method for obtaining pure vanadium. Consequently, this method can be used on an industrial scale.

This method of producing vanadium pentoxide with carbon in a vacuum is also employed in work [25]. The original materials are vanadium pentoxide containing 99.9% $V_2O_5$ and acetylene black. Reduction of the briquettes pressed from the reaction mixture takes place in three stages. In the first stage, the briquettes are heated to a temperature of $750^\circ$ to $1350^\circ$ for three hours at a pressure of $1 \cdot 10^{-1}$ mm Hg. The light grey product obtained contained 86-87% V and 7-8% oxygen. It was pulverized, mixed with an additional quantity of acetylene black sufficient for the carbon content to equal the oxygen content, and was once again heated for 8-10 hours at a temperature of $1500^\circ$, at a pressure of $1 \cdot 10^{-3}$ mm Hg. After the second stage of reduction, the product contained 96-97% V, 1.0-1.5% C, and 2-3% O, was silver-grey in color and had a metallic luster, and was very difficult to pulverize. After the addition of the appropriate quantity of acetylene black to the pulverized second stage product, the mixture was heated for 12 hours at a temperature of from $1500^\circ$ to $1700^\circ$ with a pressure of $1 \cdot 10^{-5}$ mm Hg at the conclusion of the process. The final product contained 99.6% V,

0.12% C, and 0.06% O and had a hardness $H_v$ = 50.

The weight of metal obtained corresponded to a yield of more than 95%.

The extraction of metallic vanadium by reducing its chlorides and oxychlorides with magnesium, sodium, or hydrogen was known long ago. As has already been noted, Hunter and Jones obtained high-purity vanadium by reducing its trichloride with sodium. Döring [30] obtained very pure vanadium in finely powdered form by the reaction:

$$VCl_3 + 1\frac{1}{2} H_2 = V + 3HCl.$$
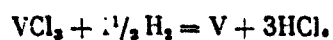
$VCl_3$ in a platinum combustion boat is placed in a platinum tube through which, when the tube is heated to a temperature of 900°, pure, dry hydrogen passes until the evolution of hydrogen chloride ceases.

The following can be used as preparative methods for obtaining 99.5% pure vanadium in powder form.

1. Two grams of $VCl_2$ and 1 gram of Mg are pressed into tablets which are placed in magnesium oxide combustion boats in a quartz tube and heated for 1-2 1/2 hours at a temperature of 700° in hydrogen or argon.

Fig. 5. Relationship between hydrogen and oxygen contents (in % by weight) in metal obtained. 1) mm Hg.

2. $VCl_4$ vapor is passed above magnesium shavings placed in the magnesium oxide combustion boat. This occurs in an atmosphere of pure hydrogen and the apparatus is gradually heated to a temperature of 700° for 2 1/2 hours. The chlorides are washed out of the mixture of V, $VCl_2$, and $VCl_3$ with water and the residue is powdered vanadium.

The reduction of chlorides and oxychlorides does not always give good results because of incomplete reduction and because of the hygroscopicity of the initial products; however, this method has long been used as a "laboratory" method of obtaining vanadium [30-32].

Two years ago, in England, vanadium was industrially produced by the reduction of vanadium from $VCl_3$ with magnesium at a temperature of $840^\circ$ in an argon atmosphere [14]. Vanadium trichloride was obtained by the chlorination of ferrovanadium containing 80% vanadium in a special chamber, a chlorinator. The chlorination process is accompanied by the liberation of a considerable quantity of heat and consequently requires no external heat supply after the process is begun. A mixture of $VCl_4$, $VOCl_5$, and $FeCl_3$ is obtained from chlorination. The $FeCl_3$ is removed in a special separator and the mixture of $VCl_4$ and $VOCl_3$ is condensed and is subjected to thermal decomposition to $VCl_3$ in a stream of hot inert gas. In this case, the undecomposable oxychloride is separated from the solid $VCl_3$ by distillation.

The device yields 18-20 kg of sponge vanadium during a cycle and this is separated from the magnesium chloride, while the excess of magnesium is melted in an argon atmosphere and then heated to a temperature of $900^\circ$ in a vacuum and leached. The composition of the vanadium obtained was; 99.7% V, 0.12% C, 0.005% O, 0.01% N, and 0.01% Mg [26].

The thermal decomposition of vanadium iodide according to the reaction $VI_2 \rightarrow V + I_2$ gave the best results so far as the purity of the metal formed is concerned.

It is possible to obtain a rather small quantity of metallic vanadium with an exceptionally low (less than 0.1%) content of im-

purities by this method. This method, which was first used by Van Arkel [32] for titanium, zirconium, and then for vanadium [33], consisted in the reaction of technically pure vanadium with iodine in an evacuated vessel, resulting in the formation of volatile vanadium diiodide. The diiodide is then decomposed by red-hot tungsten or vanadium wires, leaving a dense residue of highly pure vanadium.

The iodine which reacts with the technically pure vanadium containing oxygen, nitrogen, silicon, etc., in the first stage of the process, has no noticeable effect on oxides, nitrides, carbides, etc. and, consequently, none of these impurities enter the vanadium vanadium iodide.

The shortcoming of Van Arkel's method is the fact that the filament residue remaining after thermal decomposition is coarse, nonhomogeneous, and not dense.

The iodide method has recently been considerably improved [19]; a technique has been developed for obtaining a smooth, uniform residue which can be used for further mechanical processing without refounding in the form of rods. Vanadium diiodide must be heated to a temperature of 800-900° in order to obtain an adequate rate of sublimation and a uniform residue. However, in this temperature range, the diiodide does not dissociate to any great degree and, in order to push the reaction toward dissociation, it is necessary to constantly remove the liberated iodine from the reaction area. If the vanadium diiodide is extracted in the same vessel where its thermal decomposition occurs and not in separate devices, this still further promotes the production of a uniform residue.

In the experimental installation for extracting vanadium by the iodide method (Fig. 6), small pieces of crude vanadium 1 are

Fig. 6. Equipment for extracting vanadium by the iodide method.

placed on projections on the outside of a perforated molybdenum tube 2 which is inside a quartz vessel with a rounded bottom 3. This vessel is charged with approximately 800 grams of technically pure vanadium. Two 6 millimeter tungsten electrodes 5 in a uranium glass sheath 6 pass through the ground cover 4. A vapor generator 7 made of high-melting glass contains about 860 grams of iodine.

The system is evacuated to a pressure of $1 \cdot 10^{-4}$ mm Hg and is then isolated from the vacuum system 8 by a shut-off device 9 and is heated to a temperature of $900^{\circ}$. The iodine is slowly vaporized in the quartz vessel, and it reacts with the vanadium to form a diiodide. When the reaction is completed and the device is cooled to room temperature, the vapor generator is sealed off. The quartz vessel and the vanadium diiodide which it contains are again connected to the vacuum system, evacuated to $1 \cdot 10^{-4}$ mm Hg, and slowly heated to a temperature of $800-900^{\circ}$. The tungsten or vanadium filament is heated to a temperature of $1400^{\circ}$. The rate of precipitation is maintained by controlling the filament temperature. The operational regime varies from 0.6 amps and 12 v at the beginning of decomposition to 82 amps and 8 v at its end. The precipitate of extremely pure metal weighs 50 grams. The metallic regulus is refounded in an arc furnace in a pure argon atmosphere (99.92% argon) and has a Vickers hardness of 70. The regulus is rolled at room temperature into a 1 mm sheet with no intermediate tempering. The high value of

relative contraction exhibited by the vanadium is shown by its high plasticity. We will consider later the properties of vanadium obtained by the iodide method.

In addition to the thermal decomposition of vanadium diiodide, which is assumed to include the refining of technically pure vanadium, zone [34] and vacuum [35] melting by electron bombardment have recently come into use for purifying metallic vanadium. The specimen (anode) is melted by bombarding, with electrons, a cathode made of tungsten wire or strips in the form of a ring enclosing the anode.

In order to avoid contaminating the vanadium with material from the crucible, a method has been worked out for vertical, noncrucible melting. In zone melting, when the melt zone moves along the specimen, the latter is refined by three processes: 1) degasification in vacuum melting; 2) evaporation of vaporized impurities; 3) removal of impurities in the liquid phase.

Work [34] describes the manner in which the vertical, noncrucible melting of vanadium was carried out with an electron beam. The specimen was fastened to a frame which moved with a velocity of 1.25-2.25 cm/min relative to the cathode. Melting took place in a pyrex tube 50 cm long with a vacuum of $1.5 \cdot 10^{-4}$ mm Hg. The maximum specimen diameter, which was determined by surface tension and the density of the liquid phase, was 6 mm for vanadium and the standard voltage and current used to melt a specimen of this diameter was 1.5 kv and 5 ma. This method yielded single crystals of vanadium ranging from 20 mm to 1 cm in diameter and up to 16 cm in length.

Ductile vanadium, containing 99.5% vanadium can be further purified by electrolysis. It has recently been suggested [36] that this method be used to extract the very pure vanadium used as a coolant in atomic reactors. Electrolysis is carried out in an iron

crucible with a graphite lining placed in an evacuated steel chamber filled with an inert gas. The refined metal and vanadium scrap are at the bottom of the crucible and serve as an anode. A fused salt mixture of $NaCl \cdot VCl_2$ serves as the electrolyte. $VCl_2$ is also produced in the chamber by slowly chlorinating the vanadium scrap. Chlorination continues until the vanadium content in the electrolyte is brought up to 2.1%.

The current density in the iron rod which serves as a cathode is 0.3-0.0016 amps/cm$^2$, corresponding to a voltage of 0.35-1.0 v. Since the anode dissolves during electrolysis, it is necessary to add vanadium scrap to the bath lest the efficiency of the chamber be reduced and the cathode precipitate have a small-crystal form with a considerable quantity of occluded salts.

The yield of regenerated, purified metal was 87% of the metal charge; the hardness of the vanadium crystals obtained varied between three and 90 on the Rockwell scale.

Thus, there are basically three contemporary methods of obtaining plastic vanadium, not including refining:

1) reduction of $V_2O_5$ and $V_2O_3$ with calcium in a vacuum;

2) reduction of $V_2O_3$ with carbon in a vacuum;

3) reduction of the chlorides and oxychlorides with magnesium, sodium, and hydrogen.

Only the first of these methods is used industrially, but both the first and second methods hold the promise of making ductile vanadium as available a metal as tungsten, molybdenum, etc., in the near future.

Data on certain physical properties of various vanadium compounds used to obtain pure vanadium, as well as carbides and nitrides [37], and the most common phases in metallic vanadium are given

TABLE 2

Physical Properties of Vanadium Compounds

| 1 Формула | 2 Цвет, состояние, кристаллическая форма | 3 Удельный вес | 4 Температура плавления, °C | 5 Температура кипения, °C | 6 Теплота образования, ккал/моль |
|---|---|---|---|---|---|
| $V_2O_3$ | Черный, кристаллический, структура корунда | $4,87^{18}_4$ | 1970 | — | 302 ± 10 |
| $V_2O_5$ | Оранжевый ромбический | $3,357^{18}_4$ | 690 | 1750 | 437 ± 7 |
| $VCl_2$ | Зеленовато-слюдянистый, гигроскопичен, пластинки гексагональны | $3,23^{18}$ | — | — | 147 ± 4 |
| $VCl_3$ | Розовые кристаллы, расплывающиеся в коричневую жидкость | $3,00^{18}$ | — | — | 187 ± 8 |
| $VCl_4$ | Красно-бурая дымящая жидкость, разлагается водой и на воздухе | $1,832^{18}$ | 28+2 | 148, 5 (755 мм) | 165 ± 4 |
| $VOCl_3$ | Прозрачная светло-желтая жидкость | $1,854^{18}$ | −78,9 ± 0,2 | 127,20 (760 мм) | 200 ± 4 |
| $VJ_2$ | Темно-фиолетовые гексагональные листочки кристаллизуются по типу $GdJ_2$, гигроскопичны | 5,44 | — | — | — |
| $VJ_3$ | Коричнево-черный кристаллический продукт, гигроскопичен | 4,2 | — | — | — |
| $V_2C$ | Темный, кристаллический, гексагонален, компактен | 19,75 расчетная | — | — | — |
| VC | Темный, кристаллический, гранецентрированный кубический | 5,48 | 2830 | — | 28,0 |
| $V_3N$ | Темно-серый, кристаллический, гексагонален, плотная упаковка | 5,967 | — | — | — |
| VN | Серо-коричневый, кристаллический, гранецентрированный, кубический | 6,040 | 2055 2320 | — | 60,0 ± 2,0 |

1) Formula; 2) color, state, crystal shape; 3) specific weight; 4) melting point, °C; 5) boiling point, °C; 6) heat of formation, kcal/mole; 7) black, crystalline, corundum-type structure; 8) orange, rhombic; 9) greenish-micaceous, hygroscopic, hexagonal sheets; 10) rose-colored crystals distributed in a brown liquid; 11) red-brown fuming liquid, decomposes in water and air; 12) transparent light yellow liquid; 13) dark violet hexagonal sheets crystallized after the fashion of $GdI_2$, hygroscopic;

14) brown-black crystalline produce, hygroscopic; 15) dark, crystalline, hexagonal, dense; 16) dark, crystalline, face-centered cubic; 17) dark grey, crystalline, hexagonal, densely packed; 18) grey-brown, crystalline, face-centered, cubic; 19) calculated.

## The Properties of Metallic Vanadium

The metallic vanadium first obtained by Roscoe contained about 96% vanadium and was extremely brittle. In the history of the extraction of pure metals, a similar phenomenon may be noted for

titanium, zirconium, uranium, and even for chromium. In the first
stages of obtaining these metals, they were brittle and hard because
of their high content of detrimental impurities.* In 1927, by the
reduction of vanadium pentoxide with calcium ($V_2O_5$ + 5 Ca = 5CaO +
+ 2V), high-purity metal was obtained, containing 99.3-99.8% V,
0.06-0.05 Si, 0.20-0.24 Fe [20]. Metal having this chemical com-
position was ductile and sufficiently soft. Unfortunately, the authors
of work [20] did not give the mechanical properties of the vanadium
which they obtained but this work, published 100 years after the
discovery of vanadium, shed new light on the physical nature of van-
adium and completely changed the previously held notion that it was
a very brittle, nonplastic metal.

Metallic vanadium is greyish-white in color, does not decom-
pose water, does not oxidize in air at ordinary temperatures, and
when strongly heated combines vigorously with oxygen, chlorine,
bromine, nitrogen, sulfur, and phosphorus. The metal is capable of
absorbing a considerable quantity of hydrogen but does not form
definite compounds in this case. Vanadium is insoluble in hydro-
chloric acid, is highly soluble in nitric acid and hydrofluoric
acid, is unaffected by alkali solutions, and dissolves in molten
alkalis with the formation of vanadates.

The first data on the properties of metallic vanadium were in-
correct, because of its insufficiently high purity, and only when
new methods for obtaining very pure vanadium containing less than
0.08% impurities were worked out was it possible to consider these

*The lack of sufficient information in the scientific and technical
literature on the extraction of pure metals, including pure vanadium
which has good plastic properties, served as the vexing cause of
the fact that the Bol'shaya Sovetskaya Entsiklopediya [Great Soviet
Encyclopedia], in the 1951 edition, Volume VI, in the article on
vanadium, noted that vanadium is "a brittle and very hard metal."

## The Physicochemical and Mechanical Properites of Vanadium

| | |
|---|---|
| Atomic number | 23 |
| Atomic weight | 50.95 |
| Atomic diameter | 2.69 |
| Isotopes | 47, 48, 49, 50, 51, 52 |
| Electronic configuration | $1s^2 2s^2 2p^6 3s^3 3p^6 4s^2 3d^3$ |
| First ionization potential | 6.8 ev |
| Content in Earth's crust, % | 0.02 |
| Crystal structure up to $1550^\circ$ | body-centered cube |
| Lattice constant, A (Angstroms) | 3.034 |
| Specific weight at $20^\circ$ | 5.8 |
| Melting point, $^\circ C$ | $1900 \pm 25$ |
| Heat of fusion, kcal/mole | 4185 |
| Entropy of fusion, kcal/degree | 2.1 |
| Boiling point, $^\circ C$ | 3000 |
| Volatility at melting point | very slight |
| Heat capacity at constant pressure over temperature interval $20\text{-}100^\circ$, kcal/g·deg | 0.120 |
| Thermal conductivity ratio, kcal/cm·sec, at $100^\circ$ | 0.074 |
| The same, at $500^\circ$ | 0.088 |
| Coefficient of linear expansion ($200\text{-}1000^\circ$) | $8.95 \cdot 10^{-6}$ |
| Specific electrical resistance at $20^\circ$, ohm-cm | $26 \cdot 10^{-6}$ |
| Temperature coefficient of specific electrical resistance ($25\text{-}100^\circ$) | $2.8 \cdot 10^{-3}$ |
| Magnetic susceptibility | $1.4 \cdot 10^{-6}$ |
| Hardness (Vickers) | |
|     Iodide method | 70 |
|     Calcium-thermal method | 143 |
| Iodide method (cold rolled) | 120 |
| Modulus of elasticity, $kg/mm^2$ | 14,070 |
| Shear modulus, $kg/mm^2$ | 4730 |
| Ultimate strength, $\sigma_v$, $kg/mm^2$ | 22.2 |
| Limit of proportionality, $kg/mm^2$ | 8.5 |
| Yield point, $\sigma_s$: 0.1 $kg/mm^2$ | 10.7 |
|     0.2 $kg/mm^2$ | 11.6 |
| Relative elongation, specimen length, 2.54 cm, % | 38-40 |
| Necking, specimen length, 2.54 cm, % | 64-80 |
| Temperature region of recrystallization, $^\circ C$ | 650-800 |

properties as established.

The basic properties which we considered above were for vanadium of 99.7-99.9% purity. The physical properties given were based on works [2, 33, 20] and the mechanical properties on work [19] for very pure vanadium iodide which was cold-rolled with a 90% reduction and then tempered at a temperature of 800°. Pure vanadium has low ultimate strengths, high plasticity, a low specific weight, high resistance to corrosion, and a high melting point and in this respect resembles titanium and zirconium.

The ultimate strength of vanadium is sensitive to the presence of impurities and varies from 22 $kg/mm^2$ for vanadium iodide to 56 $kg/mm^2$ for industrial types of vanadium extracted by the calcium-thermal method. The most important property of vanadium is its ability to remain strong when heated, even to a temperature of 900°. At this temperature the ultimate strength of the unmelted vanadium is 10.5 $kg/mm^2$ [14, 38].

It is assumed that vanadium has three allotropic forms, two of which (high-temperature and low-temperature) were recently discovered and have not been sufficiently verified experimentally by us. The alpha-type has a body-centered cubic lattice and exists from room temperature to 1500°.

Seybolt and Samsion [16] in measuring the electromotive force of a vanadium-molybdenum thermocouple as a function of temperature, discovered a high temperature form of vanadium. The electromotive force curve of a vanadium-molybdenum thermocouple as a function of temperature, has a point of flexion at 1530 ± 10° (Fig. 7). However, there has as yet been no data given in the literature on the structure of this form.

Rostoker and Yamamoto [39] discovered a low-temperature form

of vanadium which exists between −33 and −25° and has a body-centered tetragonal lattice.

In comparison with such metals as copper, aluminum, and iron, vanadium exhibits higher electrical resistance and lower thermal conductivity. The linear coefficient of thermal expansion for vanadium is also low in comparison with other metals.

The mechanical properties of vanadium depend to a considerable degree on the composition and degree of purity of the metal. Since very pure vanadium in quantities sufficient for study of its mechanical properties has been obtained only recently, not all these properties have been studied with sufficient thoroughness. The most interesting information on the mechanical properties of pure vanadium is given in Reference [2].

Fig. 7. Electromotive force of a vanadium-molybdenum thermocouple as a function of temperature. 1) emf, mv.

The following properties of metallic vanadium produced by the calcium-thermal method were studied: ultimate strength, strength at elevated temperatures, toughness, temperature of transition from plastic to brittle state, and hardness. The influence of oxygen, nitrogen, and carbon on the properties enumerated above was also studied. It was established that carbon did not have so great an effect on ultimate strength, hardness, and plasticity as did oxygen and nitrogen. The total impurities due to the latter should not exceed 0.16%, so that the metal can be rolled at room temperature with a reduction of up to 90% without intermediate tempering. The

mechanical properties of vanadium vary as a function of the impurities present (Table 3), the temperature (Table 4), and the type of heat treatment (Table 5).

TABLE 3

Effect of Impurities on the Mechanical Properties of Vanadium.

| Содержание примесей, % | | | Предел прочности, кг/мм² | Удлинение при длине образца 2,5 мм, % | Сужение, % |
|---|---|---|---|---|---|
| C | O | N | | | |
| 0,25 | 0,09 | 0,08 | 58,73 | 10 | 25 |
| 0,12 | 0,18 | 0,10 | 28,00 | — | — |

1) Content of impurity, %; 2) ultimate strength, $kg/mm^2$; 3) elongation with specimen length of 2.5 mm, %; 4) reduction in area, %.

TABLE 4

Effect of Temperature on Mechanical Properties of Vanadium [content of impurities (%): C — 0.002; O — 0.085; H — 0.0068; N — 0.11]

| Температура, °C | Предел прочности, кг/мм² | Удлинение при длине образца 2,5 мм, % | Сужение, % |
|---|---|---|---|
| 22 | 63,84 | 22 | 48 |
| 400 | 69,44 | 19 | 58 |
| 600 | 28,00 | 38 | 87 |
| 800 | 16,10 | 36 | 89 |
| 1000 | 4,98 | 50 | 99 |

1) Temperature, $°C$; 2) ultimate strength, $kg/mm^2$; 3) elongation with specimen length of 2.5 mm, %; 4) reduction in area, %.

Hydrogen, just as oxygen and nitrogen, is a detrimental impurity in vanadium. It detracts from the plastic properties of the metal. When the hydrogen content reaches 0.045%, vanadium becomes very brittle. The hydrogen-induced brittleness of vanadium is sharply manifested at room temperature but decreases when the temperature is raised or lowered, more intensively for an increase than for a decrease in temperature. This brittleness can be eliminated by heating the metal to a temperature of $400°$ in a vacuum.

TABLE 5

Effect of Heat Treatment on the Mechanical Properties of
Cold-Rolled Vanadium Subjected to a 75% Reduction in Area
[content of impurities (%): C – 0.14; O – 0.15; H –
0.001; N – 0.08]

| Характер термичес-ной обработки [1] | Предел проч-ности, кг/мм² [2] | Удлинение при длине образца в 50 мм, % [3] |
|---|---|---|
| [4] С обжатием 75% | 79,03 | 5 |
| [5] Отожженный в ва-кууме в течение 15 мин. при температуре: | | |
| 600° . . . . | 72,45 | 14,5 |
| 800° . . . . | 53,48 | 25 |
| 915° . . . . | 50,33 | 28,0 |

1) Type of heat treatment; 2) ultimate strength, $kg/mm^2$;
3) elongation with specimen length of 50 mm, %; 4) with
75% reduction in area; 5) vacuum annealing for 15 minutes
at a temperature of:

Fig. 8. Fracture properties of
untreated vanadium as a func-
tion of temperature. 1) $kg/mm^2$.

Fig. 9. Fracture properties of
recrystallized vanadium as a
function of temperature. 1) Ulti-
mate strength under tension;
2) 0.2% yield point under ten-
sion; 3) elongation, %; 4) ten-
sion, $kg/mm^2$.

In work [14], generalizations are made from the vast experi-
ence of the author and his colleagues in research on the mechanical
properties of vanadium and its alloys.

Figure 8, in accordance with the data given in work [38], shows the fracture properties of unworked vanadium with a composition of 0.077% C, 0.056% O, 0.086% N, and 0.002% H. The fracture properties of processed vanadium in the temperature range from −195 to +1227° are studied in detail in work [40].

Metal which has been fused in an arc furnace and then cast is subjected to hot rolling in a soft steel jacket at a temperature of 900° and then cold rolled from 5 to 0.5 mm with intermediate vacuum tempering at a temperature of 300° for half an hour. The rolled sheet has the following content of impurities (percent by weight);

$$
\begin{array}{ccccccc}
O & N & H & C & W & Fe & Si \\
0.057 & 0.07 & 0.0004 & 0.09 & <0.02 & <0.005 & <0.005
\end{array}
$$

Specimens for tension testing were cut from a strip parallel to the direction of rolling and tested after cold rolling (Table 6) and after recrystallization at a temperature of 1000° for one hour (Fig. 9).

Table 6.
Mechanical Properties of Rolled Vanadium

| 1 Температура испытания, °C | 2 0.2% предел прочности, кг/мм² | 3 Предел прочности, кг/мм² | 4 Относительное удлинение при разрыве, % |
|---|---|---|---|
| 27 | 71,93 | 73,5 | 0,8 |
| 227 | 61,38 | 61,88 | 0,2 |
| 427 | 54,42 | 56,10 | 0,9 |
| 727 | 23,33 | 31,90 | 4,5 |
| 1027 | 3,29 | 5,93 | 46,3 |

1) Test temperature, °C; 2) 0.2% ultimate strength, kg/mm²; 3) ultimate strength, kg/mm²; 4) relative elongation at fracture, %.

The authors of work [40] came to the conclusion that vanadium has fracture properties which depend on temperature in a manner characteristic of metals with a body-centered lattice structure. Certain peculiarities of this dependence are indicated by the fact that the  strength of the metal depends on temperature in the low-

temperature region, while the yield point implies mechanical aging, a fact verified by the minimum on the expansion curve and a maximum on the ultimate strength curve at approximately $427°$.

TABLE 7

Corrosion Properties of Vanadium.

| Среда | Скорость коррозии (толщина пленки за месяц, см) | | |
|---|---|---|---|
| | литой | прокатанный | отожженный |
| 60% HCl — 70° с пропусканием воздуха через раствор | — | 0,00182 | 0,00183 |
| 20% HCl, то же | 0,1905 | 0,01421 | 0,0143 |
| 10% H₂SO₄, » | — | 0,00165 | 0,00150 |
| 20% HCl — 70° с пропусканием азота через раствор | — | 0,03120 | 0,01393 |
| 10% H₂SO₄, то же | — | 0,000915 | 0,00914 |
| 37% HCl — комнатная температура без пропускания газа через раствор | — | 0,00737 | 0,006600 |
| 10% H₂SO₄ — кипящая | 0,01219 | 0,00787 | 0,00914 |
| 85% H₃PO₄ — кипящая | — | Растворяет [18] | |
| Концентрированная HNO₃ — комнатная температура | Растворяет [18] | Растворяет [18] | |
| 5% FeCl₃ + 10% NaCl — комнатная температура | — [19] | 0,182 | 0,1905 |
| 20% NaCl (брызги) | Не влияет | | |
| Морская вода | — | — [20] | 0,000952 |
| Промышленная атмосфера | — | Некоторое окрашивание | — |

1) Medium; 2) rate of corrosion (thickness of film after 1 month, cm); 3) cast; 4) rolled; 5) tempered; 6) 10%HCl — $70°$ with passage of air through solution; 7) 20% HCl, the same; 8) 20% HCl — $70°$ with passage of nitrogen through solution; 9) 10% $H_2SO_4$, the same; 10) 37% HCl — room temperature without passage of gas through solution; 11 11) 10% $H_2SO_4$ — boiling; 12) 85% $H_3PO_4$ — boiling; 13) concentrated $HNO_3$ — room temperature; 14) 5% $FeCl_3$ + 10% NaCl — room temperature; 15) 20% NaCl jets; 16) sea water; 17) industrial atmosphere; 18) dissolves; 19) unaffected; 20) some staining.

Because of the reactivity of vanadium, all processing and testing at elevated temperatures must be conducted in a protective atmosphere or a protective sheathing must be used. Kinzel [25] suggested the use of stainless austenite steel as a sheathing.

It should be pointed out that the metal in pure form lends itself well to hot or cold mechanical processing; it is easily pressed, ground, cut on a machine tool. stamped, extruded, welded, etc. The

plastic properties of pure vanadium are approximately the same as those of copper and nickel in this respect. The mechanical properties of vanadium after extrusion are analogous to the properties of cast iron and are characterized by low ultimate strength ($\sigma$ = 40-43 $kg/mm^2$) and considerable plasticity ($\delta$ = 33-44%; $\psi$ = 64-80%).

The properties of vanadium hardened by extrusion are studied in detail in work [41].

We should take note of the high corrosion resistance of pure metallic vanadium. Kinzel [25] summarized research in this field in the following fashion: vanadium has a high resistance to reducing acids of medium concentrations and is unstable to oxidizing agents.

Table 7 shows the results of new research on the corrosion properties of vanadium [2]. The high corrosion resistance of vanadium in air and marine environments is especially important and this, in conjunction with low specific weight and a high modulus of elasticity, makes metallic vanadium an important construction material.

## The Use of Vanadium

Vanadium has received the attention chiefly of metallurgists, being an extremely important alloying, reducing, and carbide-forming element. In this respect, metallurgy is the basic area of its use. The introduction of vanadium in the production of special types of steels has made possible the formation of thin, uniform structures, makes the steel denser, increases its toughness, elastic limit, and ultimate strength under tension and bending and extends the range of tempering temperatures.

Steel containing 0.3% C, 1% Cr, and 0.2% V, after hardening at a temperature of 900° in oil and annealing at a temperature of 400°, has the properties $\sigma_v$ = 129 $kg/mm^2$, $\sigma_s$ = 109 $kg/mm^2$, $\delta$ = 13%, while

after hardening in water and annealing at a temperature of $400^\circ$, it has the properties $\sigma_v = 144$ kg/mm$^2$ and $\sigma_s = 124$ kg/mm$^2$.

Vanadium carbides increase the hardness of steel and its resistance to abrasive and impact stresses.

Vanadium is an important additive to tool (up to 2%) and construction (up to 0.2%) steels. The successful development of heavy and transport machine building requires vanadium-manganese steels, characterized by their high resistance to impact and fatigue.

Vanadium is used for alloying steels in combination with chromium, nickel, molybdenum, tungsten, etc., and this increases the strength, hardness, and impact resistance of the products.

The addition of vanadium to low-alloy heat-resistant steel or the replacement of a portion of the molybdenum in the steel by vanadium considerably improves the mechanical properties of the steel at room temperature and its long-term strength and resistance to creep at temperatures of 470 and $590^\circ$ [42]. Table 8 shows the chemical composition of the alloys tested and Table 9 shows the fracture properties of these alloys at room temperature.

As we may conclude from Table 9, alloys B and C are the strongest. Standardization at a temperature of $1065^\circ$ markedly increases the strength of alloys with high vanadium contents and does not change the strength of alloys B and C. In this case, the plasticity of the alloys is reduced, but not so far as to preclude their technical use.

The long-term strength at a temperature of $590^\circ$ after standardization at a temperature of $980^\circ$ and annealing is highest for alloys C, B, A, and E (Fig. 10, I). Increasing the normalization temperature to 1065 and $1095^\circ$ has a positive effect on the heat-resistance of alloys with high vanadium contents (alloys F, G, E, Fig. 10).

TABLE 8

Chemical Composition of Impure Vanadium Alloys Tested, %.

| Сплав[1] | C | Si | Mn | Mo | V | Cr |
|---|---|---|---|---|---|---|
| A | 0,22 | 0,19 | 0,42 | 0,54 | — | — |
| B | 0,20 | 0,22 | 0,61 | 0,50 | 0,21 | — |
| C | 0,17 | 0,19 | 0,46 | 0,30 | 0,18 | — |
| D | 0,20 | 0,25 | 0,53 | — | 0,20 | — |
| E | 0,23 | 0,34 | 0,60 | 0,29 | 0,48 | — |
| F | 0,20 | 0,22 | 0,55 | 0,27 | 0,72 | 0,59 |
| G | 0,18 | 0,21 | 0,48 | 0,46 | 0,66 | 0,56 |

1) Alloy.

TABLE 9

Fracture Properties of Alloys at Room Temperature

| 1<br>Сплав | 2<br>Термическая обработка | 3<br>Предел прочности, кг/мм² | 4<br>Предел текучести, кг/мм² | 5<br>Относительное удлинение, % | 6<br>Сужение площади поперечного сечения, % |
|---|---|---|---|---|---|
| A | 7<br>Нормализация от температуры 982° и отпуск с температурой 676° | 48,3 | 32,2 | 38 | 63 |
| B | | 80,8 | 70,7 | 21 | 65 |
| C | | 77,0 | 56,8 | 23 | 62 |
| D | | 47,6 | 37,8 | 41 | 73 |
| E | | 58,8 | 46,9 | 30 | 73 |
| F | | 50,4 | 27,3 | 37 | 83 |
| G | | 49,7 | 24,5 | 39 | 81 |
| A | 8<br>Нормализация от температуры 1065° и отпуск с температурой 676° | 48,3 | 32,9 | 33 | 64 |
| B | | 81,9 | 71,4 | 22 | 62 |
| C | | 70,7 | 51,9 | 23 | 60 |
| D | | 49,0 | 33,6 | 33 | 70 |
| E | | 72,8 | 51,1 | 25 | 64 |
| F | | 60,2 | 44,8 | 25 | 75 |
| G | | 58,8 | 35,7 | 31 | 74 |

1) Alloys; 2) heat treating; 3) ultimate strength, $kg/mm^2$;
4) yield point, $kg/mm^2$; 5) relative elongation, %; 6) re-
duction in area of cross section, %; 7) normalization at
temperature of 982° and annealing at a temperature of 676°;
8) normalization at a temperature of 1065° and annealing
at a temperature of 676°.

Thus, the molybdenum content in vanadium steels can be reduced
to 0.3T without detriment to strength at elevated normalization
temperatures.

While the metallurgical use of vanadium as an alloying material
had already begun at the end of the last century, the use of the metal

itself and its alloys in modern technology became possible only very recently — after the production of the pure metal had been mastered. Metallic vanadium and its alloys are similar to titanium and its alloys in the nature of their use, their properties, and the prospects for their use.

Rostoker studied the solubility in vanadium of 21 elements of the periodic system [43], as well as the mechanical properties of many binary and ternary alloys of vanadium [14, 38]. The greatest interest has been aroused by binary alloys of vanadium with titanium which remained plastic and possess high strength with titanium contents of up to 50% and alloys with zirconium contents of up to 3% which have higher plasticity than unfused vanadium. In the opinion of the author, multicomponent alloys based on titanium-vanadium or titanium-zirconium alloys should be of high strength and plasticity. Chromium, aluminum, and silicon are promising as third components (Fig. 11).

Fig. 10. Strength of low-alloy steel at 590° as a function of composition and normalization temperature. I) Normalization at 982°, annealing; II) normalization at 1065°, annealing; III) normalization at 1095°, annealing; 1) tension, kg/mm$^2$, 2) time until failure, hours.

A ternary alloy containing 50% titanium and 2% silicon possesses the properties $\sigma_1$ = 105 kg/mm$^2$; $\delta$ = 12.5%, and $\psi$ = 17.5%. A vanadium alloy containing 50% titanium and 5% aluminum has high long-term strength at a temperature of 300° and is no less strong than a titanium alloy and its strength to density ratio exceeds that of alloys

based on iron, cobalt, and nickel. In addition, this alloy is pre-
pared from vanadium produced by the aluminum-thermal process and
its mechanical properties do not differ from the mechanical proper-
ties of a vanadium alloy produced by the calcium-thermal method.

In general, vanadium alloys are also used as heat-resistant materials at temperatures not exceeding 673°, where the alloy rapidly begins to oxidize because of the melting of the $V_2O_5$.

Vanadium bronzes and alloys of vanadium and aluminum are used in airplane construction and ship building because of their high strength and corrosion resistance.

Fig. 11. Hardening action of aluminum, chromium and silicon as third components in a binary alloy containing 45% V and 50% Ti. 1) 50% Al; 2) 5% Cr; 3) 5% $Si_3$; 4) ultimate strength, $kg/mm^2$.

Alloys of vanadium and noble metals are used in jewelry work and dentistry. Malleable vanadium is used as an X-ray filter in tubes with chromium anticathodes in order to obtain pure α-Cr radiation.

Vanadium is successfully used as the filament in vacuum tubes because of its high temperature-strength characteristic. Vanadium filaments can now replace tungsten filaments in the iodide method of producing vanadium and this eliminates contamination of the metal with tungsten.

Each year the use of vanadium in components for high-speed jet aircraft and rockets increases, as does its use as a sheathing material for nuclear reactors and for the cladding on reactor fuel elements. Vanadium's inability to fuse with uranium and its high thermal conductivity warrant a great deal of attention.

41

The industrial use of metallic vanadium and its alloys is a recent phenomenon and engineering has consequently still not taken advantage of all the useful, physical, physicochemical, and mechanical properties of these new materials.

Table 10 shows the compositions and designations of certain multicomponent alloys containing vanadium.

For alloying steel, ferrovanadium is used. The problem of producing ferrovanadium has been solved since the revolution by the use of Kerch iron ore and Ural titanomagnetites.

Vanadium compounds are widely used in the glass and ceramics industries because of their diversity of colors, in the dye industry as mordants, in the rubber industry, and in photography. Vanadium pentoxide, as the best drying agent, is used for oil paints. Vanadium pentoxide is of great value in the chemical industry as an active catalyst in the synthesis of organic substances (acetaldehyde and acetic acid, benzaldehyde and benzoic acid, etc.) and in sulfuric acid production. Vanadium replaces platinum as the catalyst in the contact process for the production of sulfuric acid because of its low price and resistance to poisoning.

Recently, soluble arsenovanadates have been effectively used as fungicides and insecticides. In medicine, the use of vanadium revolves chiefly about the oxidizing and antiseptic properties of its compounds.

## CONCLUSIONS

Methods have now been worked out for the extracting of high-purity (up to 0.08% impurities) vanadium which is capable of undergoing various types of mechanical processing. The basic industrial method for obtaining malleable vanadium is the reduction of vanadium pentoxide or trioxide with metallic calcium. In order to obtain

TABLE 10

Composition of Certain Metallic Alloys Containing Vanadium, % by weight.

| Сплав [1] | Fe | C | Cr | Mo | W | V | Si | Ti | Al | Mn | Ni | Co | B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 Жаропрочная ферритовая сталь | Основа [2] | 0,20 | 10—12 | до0,5 [3] | до0,5 [3] | до0,8 [3] | — | — | — | — | — | — | 0,001 [3] |
| 5 Конструкционная сталь комплексного легирования | » | 0,23—0,27 | 1,18—1,38 | — | 0,49—0,73 | 0,10—0,13 | — | — | — | 1,16—1,40 | до1,0 [3] | — | до0,001 [3] |
| 6 Ферритовая сталь с высоким пределом ползучести | » | 0,02—0,15 | 0,10—3,50 | — | — | 0,05—1,0 | 0,05—1,0 | 0,05—0,4 | — | 0,05—2,0 | — | — | 0,003 0,5 |
| 7 Жаропрочная ферритовая сталь (до 650°) | » | 0,02—0,1 | 0,10—3,5 | — | — | 0,01—1,0 | 0,05—1,0 | 0,05—0,4 | — | 0,05—2,0 | до0,1 [3] | — | до0,05 [3] |
| 8 Ферритовая ж. прочная сталь (до 600°) | » | 0,15—0,50 | 0,75—2,5 | 0,2—1,0 | — | 0,2—1,0 | — | (1—6)ХС | — | 0,2—2,0 | — | — | 0,0005 0,004 |
| 9 Ферритовая жаропрочная сталь | » | 0,03—0,25 | 3,5—8,0 | 0,3—1,5 | 0,4—2,5 | 0,01—0,5 | 0,1—1,50 | 0,05—1,5 | — | 0,1—2,0 | 2,0 | — | 0,001 0,5 |
| 10 Конструкционная сталь с повышенной ударной вязкостью | » | 0,23—0,28 | 1,30—1,35 | 0,09 | до0,5 | 0,06 | 1,04—1,09 | до0,05 | — | 1,20—1,40 | до1,0 [3] | — | 0,001 |
| 11 Жаропрочная аустенитная сталь ЭИ-388 | » | 0,38—0,47 | 14,0—16,0 | 0,5—0,8 | — | 1,4—1,8 | 0,9—1,4 | Nb 1,4 | — | 6,0—8,0 | 6,0—8,0 | — | — |
| S—32 | » | 0,27 | 19 | 2,2 | — | 3,0 | 0,5 | — | — | 0,8 | 10,5 | 46,0 | — |
| 12 Деформируемый жаропрочный выше 800° (опытный сплав) | | 0,8 | 20 | 2,0 | — | 2,8 | до0,5 | Nb 1,2 | — | 1,0 | 12 | 2,45 (основа) | — |
| 13 Деформируемый жаропрочный выше 800° (сплав с ураном) L = 117 | | 0,3 | 19,5 | 1,97 | U 2 | 2,12 | 0,35 | — | — | 0,83 | 11,8 | 2,44,3 (основа) | — |
| 14 Деформируемый жаропрочный (кобальтовый) выше 800° | | до 0,35 | 15—20 | — | W 10—15 | — | до1,0 | Nb+Ta+Ti+V от 0,5 | до 3% | до2,0 | 0,15—20,0 | 25—45 | N 0,05—0,25 |
| 15 Деформируемый жаропрочный сплав до 500° (титановый) | | — | — | — | — | 4 | — | 2 Основн | 6 | — | — | — | — |

1) Alloys; 2) base; 3) up to; 4) heat-resistant ferrite steel; 5) construction steel, complex alloying; 6) ferrite steel with a high creep limit; 7) heat-resistant ferrite steel (up to 6500); 8) heat-resistant ferrite steel (up to 6000); 9) heat-resistant ferrite steel; 10) construction steel with increased toughness; 11) heat-resistant EN-388 austenite steel; 12) deformable steel, heat-resistant above 800° (experimental alloy); 13) deformable steel heat-resistant above 800° (alloy with uranium, L = 117); 14) deformable steel (cobalt) heat-resistant above 800°; 15) deformable steel (titanium) heat-resistant up to 500°.

small quantities of extremely pure vanadium, the thermal decomposition of vanadium diiodide is employed. The latter method may still be considered among the laboratory methods for obtaining pure metals. Vanadium has now become an easily available and important metal in engineering rather than the expensive metal and laboratory curiosity which it once was.

The basic properties of extremely pure vanadium (low specific weight in conjunction with considerable strength and high plasticity, corrosion resistance) make it a valuable basis for construction and corrosion-resistant materials.

Recently, malleable vanadium has been used not only as the basis for new alloys, but also for special-purpose applications because of its peculiar physical properties. The solution of the problem of obtaining very pure vanadium and the determination of its properties have opened up great prospects for its use in the most diverse branches of engineering.

## REFERENCES

1. W. Mellor. A Compre. Treaty on Inorgan. Theoret. Chem., 9, Lond.-N.Y., 1952.

2. C.H. Hampel. Rare Metals Handbook. N.Y., 1953.

3. J. Ment, H. Daken, E. Roberts, Rare Metals, Lond., 1949.

4. Gornyy zhurnal [Mining Journal], 1834, No. 6.

5. Gornyy zhurnal, 1839, No. 5.

6. D.I. Mendeleyev, Osnovy khimii [Principles of Chemistry], Vol. II, 1946.

7. A.Ye. Fersman, Izbr. tr. [Selected Works], Vol. II, 1953, p. 452.

8. V.I. Vernadskiy, Izbr. tr., Vol. II, Izd-vo AN SSSR [Publishing House of the Academy of Sciences USSR], 1955.

9. A.G. Betekhtin, Kurs mineralogii [Course in Mineralogy], Gosgeolotekhizdat [State Scientific and Technical Publishing House for Literature on Geology and the Conservation of Mineral Resources], 1956.

10. V.P. Yelyutin, A.Yu. Pavlov, B.Ye. Levin, Ferrosplavy [Ferro-alloys], Metallurgizdat [State Scientific and Technical Publishing House for Literature on Ferrous and Nonferrous Metallurgy], 1951.

11. M.N. Sobolev, Izvlecheniye vanadiya i tatana iz ural'skikh titanomagnetitov [The Extraction of Vanadium and Titanium from the Ural Titanomagnetites], ONTI [United Scientific and Technical Publishing Houses], Moscow — Leningrad, 1936.

12. Redkiye metally kapitalisticheskikh stran. Statist. sprav. [Rare Metals of the Capitalist Nations. Statistical Handbook], Moscow, Izd-vo TsNIITsVETMET [Publishing House of the State Scientific Research Institute for Nonferrous Metals], 1958.

13. The Mining Journal. An. Rev., 1957.

14. W. Rostoker. The Metallurgy of Vanadium, N.Y., 1958.

15. D.A. Kunayev, Pravda, 24 February 1956.

16. A Seybolt, H. Samsion, J. Metals, 1953, 5 (2), sec. 2.

17. S. Bitti. J. Metals, 1952, 4 (9), 987.

18. R. McKechnie, A. Seybolt, J. Electrochem. Soc., 1950, 97, 311.

19. J. Nash. J. Electrochem. Soc., 1953, 100, 6, 272.

20. J. Marden, M. Rich. Industr. Eng. Chem., 1927, 19, 786.

21. M.F. Joly. Second International Conference of the Peacetime Uses of Atomic Energy Held at Geneva. France, 1958 (Paper 1274).

22. E. Gregory. W. Lilliendahl. J. Electrochem. Soc., 1951, 98, 10, 395.

23. C.J. Turner, L.R. Williams. Second International Conference

of the Peacetime Uses of Atomic Energy, held at Geneva, Kingdom, 1958 (Paper 44).

24. A. Beard, D. Crooks. J. Electrochem. Soc., 1954, 101, 12.

25. A. Kinzel. Metals Progress, 1950, 58, 815.

26. H.A. Wilhelm, J.R. Long. American Patent 2700606, January, 1955.

27. T. Merriel. J. Metals., 1958, 10 (9), 618-621.

28. R.A. Karasev, V.I. Kashin, M.S. Makunin, A.Yu. Polyakov, A.M. Samarin, Izv. AN SSSR, OTN [Bulletin of the Academy of Sciences USSR, Department of Technical Sciences ],1956, No. 4.

29. A.Yu. Polyakov, Vakuumnyy metod polucheniya kovkogo vanadiya [The Vacuum Method of Extracting Malleable Vanadium] in the collection Primeneniye vakuuma v metallurgii [The Use of Vacuums in Metallurgy], Izd-vo AN SSSR, 1958, pp. 147-154.

30. Th. Doring, J. Geiln. Z. anorg. Chem. [Journal of Inorganic Chemistry], 1934, 221, 56.

31. Rukovodstvo po preparativnoy neorganicheskoy khimii [Handbook of Preparative Inorganic Chemistry], edited by G. Bauer, Izd-vo Inostr. lit., [Publishing House of Foreign Literature], 1956.

32. A.E. Van-Arkel, Metallwirtschaft [Metals Economy], Vol. 13, 1934, 405.

33. A.E. Van-Arkel, Reine Metalle [Pure Metals], Berlin, 1939.

34. A. Calwerley. Scientific Instrum., 1957, 34, 4, 142.

35. R. Hagh, R. Smith. Vacuum Metallurgy, N.Y. — London., 1957, 221.

36. D.D. Blue, D.H. Baker. Second International Conference of the Peacetime Uses of Atomic Energy held at Geneva. USA, 1958 (paper 698).

37. G.V. Samsonov, Ya.S. Umanskiy. Tverdyye soyedineniya tugo-

plavkikh metallov [Solid Compounds of High-Melting Metals], Moscow, Metallurgizdat, 1957.

38. W. Rostoker. Trans. ASM, 1956, 48, 560.

39. W. Rostoker, A. Yamamoto. Trans. ASM. 1955, 47, 1002.

40. J.W. Pagh. J. Metals, 1957, 9, 10, 1243.

41. C. Lacy, C. Beck. Trans. ASM, 1956, 48, 580.

42. P. Shahinian, J. Lane. Iron Age, 1957, 180, No. 5, 91, 95.

43. W. Rostoker, A. Yamamoto. Trans. ASM, 1954, 46, 1130.

# THE METALLOCHEMISTRY OF VANADIUM

By I.I. Kornilov and N.M. Matveyeva

Metallochemistry is the study of the metallic elements of the periodic system as react with each other and with the metalloids with which they form metallic-type bonds [1, 2].

The most important task of metallochemistry is the establishment of general quantitative relationships governing the formation of the different classes of solid solutions and metallic compounds of constant and varying composition which generally do not obey the rules of valency. This problem has been solved by the use of the periodic law and the study of equilibria. The specific purpose of metallochemistry is the study of equilibria and the construction of structural diagrams of metallic systems whose nature can be predicted by the established quantitative relationships governing the formation of solid solutions and compounds by various metals.

Recently, in addition to the continuation of studies of the reactions of such widely known metals as iron, nickel, and aluminum, research has begun on phase diagrams for the rare metals, including vanadium.

Metallic vanadium in pure form was not obtained until 100 years after its discovery. This was the chief obstacle in research on the physical and physicochemical properties of pure vanadium and on phase diagrams for metallic systems based on vanadium. The pure metallic vanadium which has recently been obtained is characterized

by high corrosion resistance, plasticity, and considerable strength; this, in conjunction with its low specific weight and high melting point, make vanadium an important base for special and technical alloys for various branches of industry, including the chemical industry.

The solution, in the 1950's, of the problem of industrial extraction of pure vanadium and the demands of new branches of engineering for new materials made it possible for us to set ourselves the task of a systematic study of the chemical reactions of vanadium with various elements and of the construction of phase diagrams. The work of Rostoker [3] must be considered as the beginning of the systematic study of the reactions of vanadium with other elements. Rostoker studied the solubility in vanadium of twenty-one elements of the periodic system and proposed phase diagrams for the systems which he studied.

The problem of the reactions of vanadium with other elements can be solved by the general quantitative relationships governing the formation of metallic solutions and compounds established by the work of Yum-Rozeri [4], N.V. Ageyev [5], I.I. Kornilov [6], et al. The formation of solid solutions is governed by the following conditions:

1) the similarity of the chemical properties of the metals, as determined from their positions in the periodic system;

2) a small difference in the atomic radii of the elements, not exceeding 8-10% for the formation of saturated solid solutions and 14-18% for unsaturated solid solutions;

3) an isomorphous crystal structure for the formation of saturated solid solutions.

Metallic compounds are formed when the difference between the

chemical properties of the elements increases to the transition

points from intermediate semiconductor-type compounds to ionic-type

compounds.

The aforementioned conditions for the formation of solid solu-

tions and metallic compounds have repeatedly been verified in con-

siderations of the solubility of elements of the periodic system

in iron, nickel, chromium, and titanium [6-10].

These same quantitative relationships apply to the study of

the formation of solid solutions and compounds of vanadium.

An analysis of the differences in atomic diameter between

vanadium and the elements of the periodic system (Table 1) makes

it possible to draw general conclusions concerning the nature of

the reactions of vanadium with many elements of the periodic system.

Alkali and alkali-earth metals have larger atomic diameters

than vanadium. In Group I, this difference increases from 16.3%

for lithium to 100.7% for cesium and in Group II it increases from

16.3% for beryllium to 66.5% for barium. This large difference in

atomic diameters explains the fact that there is no reaction, metal-

lic in nature, between these elements (with the exception of lithium

and beryllium). These electropositive metals form neither solid

solutions nor metallic compounds with vanadium.

The absence of a similar reaction explains the use of sodium,

magnesium, and calcium as the most active elements in the reduction

reactions of vanadium compounds and in the extraction of pure vana-

dium which does not contain impurities of these elements.

As the elements approach the group which contains vanadium,

their chemical properties become more similar to those of vanadium

and the difference between their atomic diameters and that of

vanadium decreases.

## TABLE 1

Differences in Atomic Diameters Between Elements of the Periodic System and Vanadium.

| 1 Группа | 2 Элемент | 3 Атомный диаметр | 4 Различие, % | 1 Группа | 2 Элемент | 3 Атомный диаметр | 4 Различие, % |
|---|---|---|---|---|---|---|---|
| 5 Подгруппа А | | | | | | | |
| I | H | 1,20 | 55,3 | VIII | Fe | 2,54 | 5,5 |
| I | Li | 3,13 | 16,3 | VIII | Co | 2,50 | 7,05 |
| I | Na | 3,85 | 42,6 | VIII | Ni | 2,49 | 7,42 |
| I | K | 4,76 | 71,7 | VIII | Ru | 2,57 | 0,74 |
| I | Rb | 5,40 | 100,7 | VIII | Rh | 2,68 | 0,37 |
| I | Cs | 5,40 | 100,7 | VIII | Pd | 2,75 | 2,22 |
| | | | | VIII | Os | 2,70 | 0,37 |
| II | Be | 2,25 | 16,3 | VIII | Ir | 2,71 | 0,74 |
| II | Mg | 3,20 | 18,9 | VIII | Pt | 2,88 | 7,05 |
| II | Ca | 3,93 | 45,9 | | | | |
| II | Sr | 4,29 | 59,4 | 5 Подгруппа B | | | |
| II | Ba | 4,48 | 66,5 | | | | |
| II | Ra | — | | I | Cu | 2,55 | 5,2 |
| | | | | I | Ag | 2,883 | 7,05 |
| III | B | 1,94 | 27,9 | I | Au | 2,877 | 6,7 |
| III | Al | 2,80 | 4,08 | | | | |
| III | Sc | 3,02 | 12,2 | II | Zn | 2,748 | 22,2 |
| III | V | 3,62 | 34,6 | II | Cd | 3,042 | 13,1 |
| | | | | II | Hg | 3,10 | 15,2 |
| IV | Ti | 2,93 | 8,2 | | | | |
| IV | Zr | 3,19 | 18,6 | III | Ga | 2,74 | 1,86 |
| IV | Hf | 3,17 | 17,8 | III | In | 3,138 | 16,6 |
| IV | Th | 3,60 | 33,8 | III | Tl | 3,427 | 27,4 |
| | | | | | | | |
| V | V | 2,69 | — | IV | C | 1,54 | 42,8 |
| V | Nb | 2,94 | 9,3 | IV | Si | 2,34 | 13,01 |
| V | Ta | 2,94 | 9,3 | IV | Ge | 2,78 | 3,3 |
| | | | | IV | Sn | 3,168 | 17,8 |
| VI | Cr | 2,57 | 4,46 | IV | Pb | 3,494 | 29,8 |
| VI | Mo | 2,80 | 4,08 | | | | |
| VI | W | 2,82 | 4,82 | V | N | 1,42 | 47,2 |
| VI | U | 2,81 | 4,46 | V | P | 2,20 | 18,2 |
| | | | | V | As | 2,80 | 4,08 |
| VII | Mn | 2,60 | 3,3 | V | Sb | 3,228 | 2,0 |
| VII | Re | 2,75 | 2,2 | V | Bi | 3,640 | 35,2 |

1) Group; 2) element; 3) atomic diameter; 4) difference, %; 5) subgroup.

In Group III, aluminum is most similar to vanadium with respect atomic diameter and ytterium is least similar. It can consequently be assumed that aluminum has maximum solubility in vanadium, and ytterium, minimum solubility.

Data in the literature confirms the high solubility of aluminum in vanadium.

Beginning with Group IV, and especially in the series of elements encompassed by the long period IV from Group IV to Group VIII,

we have the greatest similarity to the atomic diameter of vanadium. This series of elements, with crystal structures identical to that of vanadium and atomic diameters differing from that of vanadium by 5-6%, can form saturated solid solutions with the latter. These elements include Ti (β-form), Nb, Ta, Cr, Mo, W, and Fe (α-form). The possibility of forming saturated solid solutions of these elements in vanadium was predicted in 1950 [6].

Experimental confirmation of many of these hypotheses has now been obtained. Certain elements of these groups are very similar to vanadium with respect to atomic diameter but are not isomorphic to it in structure. This is the reason for the formation of only unsaturated solid solutions in similar systems. These include Mn, Re, Co, Ni, and all metals of the platinum group. With the majority of metals in Subgroup B, vanadium tends to yield only unsaturated solid solutions and metallic compounds. With many metalloids (B, C, N, O), it forms only very unsaturated solid solutions of the interstitial type and high-melting compounds.

In accordance with the considerations cited, let us examine the material on the reactions of vanadium with other elements, which is available in the literature. We will consider these elements in the order in which they appear in the groups of the periodic system.

Reactions with Elements of Group I

For the elements in Group I, data on reactions with vanadium is available only for hydrogen, copper, and silver.

Starting from the fact that the hardness of vanadium increases sharply when it absorbs hydrogen, certain authors assume that hydrogen forms a solid solution in vanadium, but it is not known what type of solid solution is produced in this case. The absorbed hydrogen can be liberated from the metal by heating it to a temperature

of 400° in a vacuum. This indicates the instability of vanadium hydride as a chemical compound. Vanadium hydride containing 38.6-50 atom % of hydrogen is obtained [11] by reducing $V_2O_3$ with calcium hydride in a hydrogen stream at a temperature of 1175° for 45 minutes. This hydride is dark gray (approaching black) in color. It was first detected by Hagg in his study of the adsorption of hydrogen by vanadium when the latter was heated [12].

As has previously been noted, the alkali metals differ greatly from vanadium in chemical properties and atomic diameter. Consequently, vanadium should not react with alkali metals, with the possible exception of lithium. This phenomenon is used to obtain pure vanadium by the reduction of its chlorides with, for example, metallic sodium.

Of the elements in Subgroup B of Group I of the periodic system, copper forms an unsaturated solid solution with vanadium. Rostoker and Yamamoto computed the saturation point of copper in vanadium to be 5.5-8 atom % Cu [3]. It is assumed that there is an area of stratification on a copper-vanadium phase diagram, lying between 20 and 80% copper by weight, but this data must be assumed to be only tentative [9]. As far as silver is concerned, there is only isolated data on the mutual insolubility of these two metals, both in the liquid and solid states [3]. There is no information in the literature on phase diagrams for vanadium-gold systems, but we do have data on the solubility of vanadium in gold, which comes to approximately 13 atom % at room temperature and 17.5 atom % at a temperature of 970° [13, 14].

Reactions with Elements of Group II

The metals of Group II, Subgroup A, just as the alkali metals, differ from vanadium in chemical properties and atomic

diameter and consequently should not form solid solutions with vanadium. The exception is beryllium (whose atomic diameter differs from that of vanadium by 16.3%). The saturation point of beryllium in vanadium is 0.8% by weight or 4.3 atom %. The phase diagram of a vanadium-beryllium system [3] is of the eutectic type. The eutectic point corresponds to the alloy at 49.9 atom % Be and a temperature of $1680^\circ$. A $VBe_2$ phase, isomorphous to $MgZn_2$ and having a hexagonal crystal structure, has been discovered in vanadium-beryllium systems by X-ray crystallography.

The fact that there is no reaction between magnesium and calcium, and vanadium explains the wide use of these elements in the development of a method for extracting vanadium from its compounds — chlorides, oxides, and sulfides.

The reactions of vanadium with the elements of Group II, Subgroup B — zinc, cadmium, and mercury — are not covered in the literature. Because of the considerable difference in atomic diameter and the great difference in melting and boiling points, it is difficult to assume the possibility of these elements forming solutions and compounds with vanadium.

## Reactions with Elements of Group III

Of the elements in Group III, Subgroup A, boron has the smallest atomic diameter and can yield very dilute solid solutions with vanadium, as well as forming metallic compounds with it — borides. According to the data of Reference [3], the solubility of boron in vanadium does not exceed 2 atom %. Rostoker and Yamamoto confirmed the existence of the earlier known vanadium borides (17.52% B by weight) and $VB_2$ (29.81 atom % B) by X-ray crystallography. VB has a rhombic crystal lattice of the CrB type and is formed, according to Reference [3], by a peritectic reaction of $VB_2$ and by fusion at

temperature of $1780^\circ$. $VB_2$ has a hexagonal crystal structure and is isomorphic to other diborides (Ti, Zr, Nb, Ta)$B_2$. $V_2B_5$, which is isomorphic to $Ti_2B_5$, $W_2B_5$, and $Cr_2B_5$ [15], and $V_3B_4$ have also been discovered [16].

A work was recently published [17] in which a preliminary phase diagram for a vanadium-boron system was proposed; this diagram was based on melting-point studies of the alloys, their micro-structures, and X-ray analysis (Fig. 1). The initial materials were vanadium containing less than 0.5% impurities and powdered boron containing 96% boron, 0.9% magnesium, 0.14% iron, 0.1% silicon, and a significant quantity of oxygen. The alloys were produced from powders by sintering under pressure in argon for 12 hours at a

Fig. 1. Preliminary phase dia-gram for a vanadium-boron system. 1) V, % by weight; 2) V, atom %.

Fig. 2. Phase diagram of a vanadium-aluminum system (black dots indicate points determined by experimenta-tion). 1) Al, atom %; 2) Al, % by weight.

temperature of $1600^\circ$ and by ordinary sintering in a tubular tung-sten furnace in argon for 4 hours at a temperature of $1800^\circ$. At this temperature, the alloys rich in vanadium and the alloys rich in boron are fused.

X-ray analysis confirmed the presence of the earlier known borides VB, $V_3B_4$, $VB_2$ and detected the new compound $V_3B_2$ in the vanadium-boron system. However, the presence of the earlier known compound $V_2B_3$ was not proved either in the roasted or smelted specimens. The range of concentrations in the homogeneous regions designated as borides has not been established by X-rays, but it is assumed that it must be small. Determination of melting points with a micropyrometer and the known microstructures have shown that the compounds $V_3B_2$, $VB_2$, and VB melt without decomposition, while $V_2B_4$ is formed by a peritectic reaction. The eutectic reaction $L \rightleftharpoons V_3B_2$ + + $\alpha$ occurs at a temperature of $1550^\circ$ and with 15 atom % boron. The location of the second eutectic, which is on the other side of the diagram, has not been precisely determined. As has already been shown, of the elements in Group III, aluminum is most similar to vanadium in atomic diameter. According to the data of Reference [3], the solubility of aluminum in vanadium is approximately 50 atom % of aluminum.

Figure 2 shows the phase diagram for a vanadium-aluminum system. Malleable vanadium produced by the calcium-thermal method is used to produce the alloys. In contrast to the work by Rostoker and Yamamoto [3], where alloys containing up to 70% vanadium by weight are studied, the authors of the more recent work [18] studied the entire diagram and introduced additions and corrections to the earlier proposed phase diagram. Thus, a new phase $\delta$ has been discovered, formed by a peritectic reaction between the liquid phase and the vanadium sol'd solution at a temperature of $1670^\circ$. Its composition is 54.2% by weight or 36.5 atom % of vanadium and corresponds to the formula $Al_8V_5$. This is a single phase which has a rather wide region of homogeneity. Two other phases, $\gamma(Al_3V)$ which melts incon-

gruently at a temperature of $1360^\circ$ and $\beta(Al_6V)$ which melts incongruently at a temperature of $735^\circ$, were described earlier by Rostoker and Yamamoto. The $\beta$-phase was first discovered by them. A new phase, to which the composition $Al_{11}V$ (14.6% by weight or 8.3 atom % V) can be ascribed, is formed by a peritectic reaction between the liquid and the $\beta$-phase at a temperature of $685^\circ$. This can also be considered to be a solid solution of $Al_{10}V$ and $Al_{21}V_2$. Aluminum dissolves only a very small quantity of vanadium, (0.37% by weight or 0.09 atom %) at a temperature $660^\circ$. Reference [18] did not verify the formation of a compound by a peritectic reaction at a temperature of $1215^\circ$, as was surmised by Rostoker and Yamamoto. Neither was the existence of the earlier known phases $V_2Al$, $VAl$, $V_2Al_3$, $VAl_4$, $VAl_7$ confirmed.

There is no data available which permits the construction of phase diagrams for vanadium systems involving the remaining elements of Group III of the periodic system, including the elements of the lanthanide series. It may be concluded from the fact that rather high-purity vanadium has been extracted by the reduction of its pentoxide with a mixture of metals and lanthanides that these metals do not form solid solutions with vanadium. Vanadium does <u>not</u> form solid solutions with the elements of Group III, Subgroup B — gallium, indium, and thallium — because of the difference in chemical properties and the ratio of atomic diameters.

Reactions with Elements of Group IV

The elements of Group IV, Subgroup A — titanium and zirconium — react with vanadium and form solid solutions. Titanium, the nearest neighbor to vanadium in the periodic system, has an atomic diameter which approximates that of vanadium, and, at high temperatures, it is isomorphic to the vanadium crystal lattice ($\beta$). Consequently, in

this form, it should form a continuous series of solid solutions with vanadium on crystallization. The phase diagram (Fig. 3) for a vanadium-titanium system has been studied in detail [19, 20].

The fusibility diagram has a certain minimum at 31 atom % of vanadium. Vanadium sharply reduces the temperature of the $\alpha \rightleftharpoons \beta$ polymorphic transformation of titanium and, consequently, reduces the field of the $\alpha$ phase. The two-phase region $\alpha + \beta$ (Fig. 4) extends as far as 21 atom % of vanadium at a temperature of $650^\circ$. The data given in work [19] on a vanadium-titanium phase diagram are confirmed by other data in works [3, 20]; the only discrepancy is a slight difference in the saturation point of vanadium in $\alpha$ titanium.

Fig. 3. Phase diagram of a vanadium-titanium system. 1) Ti, atom %; 2) Ti, % by weight.

Fig. 4. Two-phase region of $\alpha + \beta$-phase diagram of a vanadium-titanium (light dots indicate one phase, crosses indicate two phases). 1) V, atom %; 2) V, % by weight.

The alloys in a vanadium-titanium system in the region encompassed by 15-17% vanadium by weight are subjected to intensive precipitation hardening, with a resultant increase in hardness, decrease in plasticity, and considerable change in the crystal lattice parameters [21].

Study of a single crystal of an alloy containing 16% vanadium which was subjected to aging at a temperature of 460° for one-half hour showed reflections on the X-ray photograph of a new ω-phase whose elementary cell can be represented as a hexagonal system with the parameters a = 4.60 A and c = 2.82 A. The ω-phase is metastable. The kinetics of its formation were studied in alloys containing 15 and 17.5% vanadium by weight [22]. After diffusion annealing in the β region (900-950°) the specimens were quenched in water and then soaked at temperatures of 200-700°. In this case, an ω-phase was formed. Brief heating of the aged alloys to temperatures exceeding 550° led to virtually complete dissolving of the ω-phase. The ω-phase forms again on repeated soaking at lower temperatures, but it is proportionally smaller to the extent to which the previous soaking at the dissolution temperature of the ω-phase was greater.

Vanadium forms only unsaturated solid solutions with zirconium, in accordance with the great difference in atomic diameters. The saturation point for zirconium at a temperature of 1000° is less than 1.7 atom %, while at room temperature it is still less. Figure 5 is a phase diagram of the vanadium-zirconium system discussed in Reference [3]. While vanadium does not form compounds with titanium, the compound $V_2Zr$ is observed in a titanium-zirconium system. This compound is formed by a peritectic reaction between the vanadium solid solution and the melt at a temperature of 1740°. $V_2Zr$ is in eutectic equilibrium with the zirconium solid solution at a temperature of 1360°.

There is no information in the literature on the reactions of vanadium with hafnium. In accordance with atomic diameters, it can be assumed that hafnium, as a very close analogue of zirconium, will yield highly unsaturated solid solutions with vanadium. For

the same reason, thorium should be absolutely insoluble as a solid in vanadium. A vanadium-thorium phase diagram [23] is of the simple eutectic type (Fig. 6). The eutectic occurs at a temperature of 1400° and contains approximately 19 atom % vanadium.

Fig. 5. Phase diagram of a vanadium-zirconium system. 1) Zr, % by weight; 2) V, solid solution.

Fig. 6. Phase diagram of a vanadium-thorium system. 1) Th, % by weight; 2) Th, atom %.

Carbon and silicon — the elements in Group IV, Subgroup B — react with vanadium to form highly unsaturated solid solutions and compounds of the carbide and silicide type.

Owing to the large difference in atomic diameters, carbon forms unsaturated solid solutions with vanadium [24, 25]. The small atomic diameter of carbon, as when carbon reacts with iron, facilitates the formation of solid solutions of the interstitial type. According to the data of Schöenberg [25], the solubility of carbon in vanadium at a temperature 1000° is approximately 0.2% by weight or 1 atom %.

The carbide phases of vanadium have been studied in many works. References [3, 26] are critical surveys of these works. The authors of Reference [3] carried out independent phase research on a vanadium-carbon system containing up to 19% carbon by weight, using X-ray crystallographic, microstructural, and thermal analyses (Fig. 7).

Schönberg used 99.7% pure vanadium in order to produce alloys in a vanadium-carbon system. He detected two carbide phases, $V_2C$ and VC. The hexagonal phase $V_2C$ has a region of homogeneity from 8% C by weight or 27 atom % C to 10.5% C by weight or 33 atom % C. The VC phase has a region of homogeneity from 15.1% C by weight or 43 atom % C to 18.5% C by weight or 49 atom % C.

M.A. Gurevich and B.F. Ormond [27] studied the structure of the carbide phases of vanadium containing up to 18% C by weight and 0.14% $O_2$ by weight. The authors came to the conclusion that the carbide phases, no matter by what method they were obtained, contained a certain quantity of oxygen. Oxygen occurs in these phases in the form of oxycarbides. In addition to the known carbides $V_2C$ and VC, which were considered as oxycarbides in work [27], a new δ-phase has been discovered, having a region of homogeneity extending approximately from $VC_{0.5} = O_{0.1-0.14}$ to $VC_{0.7} = O_{0.0-0.14}$ and a cubic face-centered crystal lattice with periods 4.115-4.130 kx.

References [3, 26, 27] rejected the existence in a vanadium-carbon system of such phases as $V_5C$ and $V_4C$, which were found in this system by Osawa and Oya [28]. The work by H. Nowotny et al. [29] is devoted to vanadium carbide VC and its reaction with uranium carbide UC. VC dissolves UC very slightly; uranium carbide was discovered in an alloy containing 90 molecule % VC by X-ray crystallography. On the other hand, UC dissolves VC in quantities up to 40 molecule %, despite the considerable difference (19%) in the lattice constants of the carbides.

The solubility of silicon in vanadium at temperatures approaching the melting point of vanadium is less than 5% by weight or 6.4 atom % and at a temperature of $900^\circ$ is less than 2.5% by weight or 13 atom %. At a temperature of $1840^\circ$, according to refer-

erence [3], a eutectic reaction $L \rightleftharpoons V_{tv.r} + V_3Si$ occurs in a vanadium-silicon system, proceeding from the vanadium. A study of the microstructure of cast alloys, given in the same work, showed that a peritectic reaction occurs between the liquid phase and the $V_3Si$ at temperatures exceeding $2000°$ with the resulting formation of a new phase whose composition was not determined by the authors and which was tentatively assumed to be VSi.

In work [30], the structure and composition of the unknown silicide was established by X-ray analysis and proved to correspond to the formula $V_5Si_3$ and was isomorphic to $Ta_5Si_3$, $\beta$ $Nb_5Si_3$, $Mo_5Si_3$, and $W_5Si_3$.

Kieffer, Benesovsky, and Schmid [31] studied the vanadium-silicon phase diagram, verified the structure and composition of $V_5Si_3$, and constructed the diagram shown in Fig. 8.

Of interest are the works by the Austrian author Nowotny, which are devoted to a study of a system of silicides [30, 32] and are of great importance for research on superhard, heat-resistant materials. All the vanadium silicides shown in the vanadium-silicon phase diagrams have been obtained and silicide vapor systems have been studied.

Let us also cite from Nowotny's work the data on the nature of the reactions between vanadium silicides and silicides of other metals.

Primarily, the authors studied the volume of the elementary cell (Fig. 9) and the lattice constants (Fig. 10) and established the limits of mutual solubility for silicides.

The $VSi_2$-$TiSi_2$ system has been studied in greater detail [33]. The alloys of this system (Fig. 11) have a very high heat resistance and their addition to other alloys which are subject to intensive

oxidation on heating considerably increases their heat resistance.

Fig. 7. Phase diagram of a
vanadium-carbon system.
1) C, % by weight.

Fig. 8. Phase diagram of a
vanadium-silicon system.
1) Si, % by weight; 2) Si,
atom %.

Fig. 9. Change in volume of elementary cell in the
following systems: a) $VSi_2$-$TiSi_2$; b) $VSi_2$-$NbSi_2$,
$VSi_2$-$MoSi_2$; c) $V_5$-$Si_3$-$Zr_5Si_3$, $V_5Si_2$-$Nb_5Si_3$; 1) Mole-
cule %.

| VSi₂ | | | V₅Si₃ | | | V₃Si | |
|---|---|---|---|---|---|---|---|
| 1 непрерывные твердые растворы | 2 ограниченные твердые растворы | 3 наименьшие растворы | 1 непрерывные твердые растворы | 2 ограниченные твердые растворы | 3 наименьшие растворы | 1 непрерывные твердые растворы | 2 ограниченные твердые растворы |
| NbSi₂ | TiSi₂ MoSi₂ | ZrSi₂ | Ta₅Si₃ Nb₅Si₃ | Zr₅Si₃ | — | Cr₃Si Mo₃Si | — |

1) Saturated solid solution; 2) unsaturated solution; 3) very slight solution.

Table 2 shows the basic properties of vanadium silicides [26, 31, 33].

Work [34] is devoted to the reaction of vanadium with germanium. For the purpose of this work, alloys containing 29-83 atom % vanadium were studied by X-ray and microstructural methods. In addition to the previously known germanide $V_3Ge$, belonging to the structural type $Ge_3Si$ [35], the authors of work [34] distinguished a new compound $V_5Ge_3$, having a structure of the $MnSi_3$ type (a = =7.280 kx, c = 4.960 kx, c/a = 0.676). In rapidly cooled alloys, this compound occurs in equilibrium with germanium and the compound $V_3Ge$. In accordance with the ratio of the atomic diameters in the vanadium-germanium system, it is possible to form a solid solution of germanium in vanadium.

A tentative phase diagram for a vanadium-tin system (Fig. 12) was constructed in Reference [36] from data obtained by X-ray and microstructural analyses of ten alloys annealed at various temperatures up to 1100°. The maximum solubility of tin in vanadium (α-solid solution) is approximately 20% by weight or 10 atom %. The compound $V_3Sn$ (47.71% Sn by weight) has a cubic lattice structure with the constants a = 4.94 A [37] and is formed by the peritectic relation $L + \alpha \rightleftarrows V_3Sn$.

There is no data in the literature on the reaction of vanadium with lead. According to the ratio between the atomic diameters,

TABLE 2

Properties of Vanadium Silicides.

| Свойства | V,Si | V,Si, | VSi, |
|---|---|---|---|
| | 1 | 2 Силициды | |
| 3 Содержание кремния, % | 12 15,5 | 13 24,8 | 14 52,4 |
| 4 Структура . . . . . . . . . . . . . . . | Кубическая | Тетраго-нальная | Гексаго-нальная |
| 5 Период решетки, кх . . . . . . . . . . | | | |
| a . . . . . . . . . . . . . . . | 4,712 | 9,41 | 4,562 |
| c . . . . . . . . . . . . . . . | — | 4,74 | 6,359 |
| c a . . . . . . . . . . . . . . . | — | 0,504 | 1,394 |
| 6 Плотность экспериментальная, г/см³ . . . . | 5,67 | 4,80 | 4,71 |
| 7 Микротвердость при нагрузке 100 г, кг/мм² | 1430—1560 | 1350—1510 | 1090 |
| 8 Температура плавления, °C . . . . . . . . | 1730 | 2150 | 1670 |
| 9 Удельное электросопротивление (25°), мк·ом·см . . . . . . . . | — | — | 9,5 |
| 10 Температура перехода в сверхпроводящее состояние, °K . . . . . . . . . . . . . | 17,0 | — | -- |
| 11 Изменение веса при окислении (мг/см²) при температуре 1250° . . . . . . . . . . | 63 | —7,7 | +25 |
| 1400° . . . . . . . . . . | -- | —600 | —12 |

1) Properties; 2) silicides; 3) silicon content, %; 4) structure; 5) lattice constants, kx; 6) experimentally determined density, $g/cm^3$; 7) microhardness with 100 g load, $kg/mm^2$; 8) melting point, °C; 9) specific electrical resistance ($25^\circ$), $\mu$ohm-cm; 10) temperature of transition to superconductive state, °K; 11) change in weight ($mg/cm^2$) on oxidation at temperature of 1250°; 12) cubic; 13) tetragonal; 14) hexagonal.

Fig. 10. Change in lattice constants in the following systems: a) $V_3Si-Nb_3Si$; b) $V_3Si-Mo_3Si$, $V_3Si-Cr_3Si$.
1) Molecule %.

solid solutions should not be formed between vanadium and lead.

### Reactions with Elements of Group V

Niobium and tantalum, elements of Group V, Subgroup A, are

direct analogues of vanadium, have a crystal structure isomorphic to that of vanadium, and differ only slightly in atomic diameters. This also determines their reactions with vanadium.

While studying the problem of the formation of saturated solid solutions of metals of the transition group, one of the authors of reference [10] predicted the formation of saturated solid solutions of vanadium with niobium and of vanadium with tantalum. Later, experimental research on the alloys of a vanadium-niobium system containing up to 70% niobium by weight (Fig. 13) showed that the components of the system formed a continuous series of solid solutions. After annealing at a temperature

Fig. 11. Change in physical properties in a $VSi_2$-$TiSi_2$ system. 1) Hardness, $H_V$; 2) melting point; 3) density; 4) $H_V$, $kg/mm^2$; 5) 1/density; 6) $T_{pl}$, °C; 7) $TiSi_2$, molecule %.

Fig. 12. Tentative phase diagram of a vanadium-tin system. 1) Sn, % by weight; 2) Sn, atom %.

Fig. 13. Phase diagram of a vanadium-niobium system. 1) End of crystallization; 2) beginning of crystallization; 3) Nb, atom %; 4) Nb, % by weight.

of 900°, alloys in the region of 36 atom % niobium showed certain signs of transition to a solid state. The authors of reference [3] attributed this transition to the formation of a σ-phase which is characteristic for alloys of metals in the transition groups. The later work [38] refuted the hypothesis of the formation of some kind of phase in a niobium-vanadium system and proposed a phase diagram with a continuous series of solid solutions.

Reference [3] studied alloys containing up to 80% tantalum by weight which only formed a solid solution in the cast state. Alloys in the region of 25-80% tantalum by weight, annealed at a temperature of 900°, contain a second phase which, in accordance with the X-ray diffraction diagram, the authors included in the σ-phase series. According to our classification [39], the σ-phases formed from the solid solutions of vanadium-niobium and vanadium-tantalum systems can be related to Kurnakov compounds.

The elements of Group V, Subgroup B are markedly unlike vanadium with respect to chemical properties. Just as the metal-analogues of Group VA tend to form saturated solid solutions, so do the elements of Subgroup B tend to give a different type of compound with no noticeable regions of solid solution.

It is known that nitrogen dissolves very slightly in vanadium [3]. A cast alloy containing 1% nitrogen by weight or 2.9 atom % having a single-phase structure is characterized by an obvious two-phase structure after annealing at a temperature of 900°.

When the nitrogen content is high, vanadium nitride VN is formed. This compound has a sodium chloride structure and is similar to the oxides, carbides, and nitrides of other metals. The region of homogeneity for vanadium nitride occurs between 37.8 and 49.4 atom % nitrogen and the melting point of this compound is approxi-

mately 2050$^{\circ}$.

Reference [40] describes the discovery of a new vanadium nitride V$_3$N with a hexagonal structure and a region of homogeneity extending from 27.1 to 29.9 atom % N. It is obtained by mixing VN and powdered vanadium in stoichiometric proportions, pressing the mixture into tablets under high pressure, and heating them for 24 hours in thoroughly evacuated quartz tubes at a temperature of 100-1100$^{\circ}$ [41].

In the powdered state, vanadium nitride is of a grey-brown color with a bronze tint and is quite stable chemically, VN being more stable than V$_3$N. Vanadium forms the phosphides VP$_2$, VP, and VP $<$ 1 (some phases on the phosphorus-vanadium phase diagram) [42]. The most stable of these is VP, which is stable up to temperatures of 1056$^{\circ}$. VP$_2$ can be obtained by synthesis from its elements with an excess of phosphorus. VP is obtained by the decomposition of VP$_2$ in a vacuum at temperatures of 700-900$^{\circ}$. Vanadium phosphides are dark-grey substances (the lower members of the series having a semimetallic luster) with acid-resistant properties. The structure of VP$_2$ is similar to that of NbP$_2$ and TaP$_2$; V$_3$P is similar in structure to Ge$_3$P and (Fe, Co, W)$_3$P.

The phase diagrams for vanadium-arsenate and vanadium-antimony have not been systematically studied.

H. Nowotny and his fellow workers [43] surmised the existence of some compounds of vanadium with arsenic. They obtained one of these compounds, VAs, by heating the elements in an evacuated silicon vessel. This compound dissociates in a vacuum at temperatures exceeding 1000$^{\circ}$ to V$_2$As which melts at a temperature of 1345$^{\circ}$. The compounds VSb$_2$, isomorphic to CuAl$_2$, was obtained during the course of this work.

There is no information in the literature on the reaction of vanadium with bismuth.

Reactions with Elements of Group VI

Of the elements of Group VI, Subgroup A, chromium and molybdenum form saturated solid solutions with vanadium. This is in complete accordance with the conditions stated for the formation of saturated solid solutions in vanadium and corresponds to the predictions of one of the authors of this paper on the formation of a continuous series of solid solutions in these systems [10]. No transitions to the solid state have been discovered in the vanadium-chromium system [3, 44, 45]. Figure 14a shows the change in lattice constants for annealed alloys of the vanadium-chromium system as a function of their composition [44]. Figure 14b shows the change in lattice constants of alloys of the vanadium-molybdenum system which were annealed for 5 hours at temperatures of 1000 and 600° and slowly cooled [46]. The nature of the curve indicates that the new phase discovered earlier [3] in the microstructure of annealed alloys is not formed in the region of 10-60% molybdenum by weight.

Figure 15 is a phase diagram of a vanadium-molybdenum system constructed according to data on the change in liquidus and solidus temperatures and studies of microstructure, physicochemical properties, and plasticity [7]. The alloys were reduced from 95.5% pure vanadium produced by the aluminothermal method and 99% pure molybdenum by electric arc fusion in an argon atmosphere. Before the tests to determine their properties, the alloys were annealed in a vacuum for 10 hours at a temperature of 1600°. The method used to study the solidus and liquidus temperatures of these high-melting alloys consisted in the determination (with an optical pyrometer) of the instant at which a hole drilled into the sample closed (the

69

solidus temperature) and of the instant at which contact is broken on the melting of the specimens at a necked section (liquidus temperature).

Fig. 14. Change in lattice constants in the following systems: a) vanadium-chromium; b) vanadium-molybdenum. 1) Lattice constant, kx; 2) Cr, atom %; 3) Mo, atom %; 4) Vegard's (Wegard's) line.

Fig. 15. Phase diagram of a vanadium-molybdenum system.

As may be seen from Fig. 16, the addition of a second component sharply increases the hardness, microhardness, and specific electrical resistance of the alloys and reduces their plasticity, phenomena characteristic of a system with unlimited solubility. The microstructure of the alloys confirmed that a continuous series of solid solutions was formed in this system.

There is not sufficient data to construct a phase diagram for a vanadium-tungsten system. If we proceed from the relationship of atomic diameters, the formation of a continuous series of solid solutions in this system is predicted in reference [10].

Experimental research [3] on alloys of vanadium with tungsten which contain up to 30 atom % tungsten has established that the

solubility of tungsten in vanadium exceeds 21 atom %. But there is
no data in this work on the solubility of tungsten at temperatures
approaching the melting point of vanadium. Figure 17 is a phase
diagram of a vanadium-uranium system [47, 48]. The alloys were pro-

Fig. 16. Change in properties in a vanadium-
molybdenum system: a) specific electrical re-
sistance; b) mechanical properties; 1) hard-
ness of cast alloys ($H_p$); 2) hardness of
annealed alloys ($H_p$); 3) microhardness of
($H_\mu$); 4) plasticity ($\varepsilon_{st}$); 5) $r \cdot 10^{-6}$ ohm-cm;
6) $H_\mu$, $H_p$, Kg/mm$^2$; 7) $\varepsilon_{st}$, %.

duced in electric arc furnaces in a helium atmosphere from vanadium
iodide and pure uranium containing no more than 0.1% impurities.
The phase diagram is of the eutectic type, with the eutectic state
occurring at 18 atom % vanadium and 1040°. Vanadium reduces the allo-
tropic transition temperatures of uranium. The solubility of vanadium
in γ-uranium is 12 atom % at the eutectic temperature and it de-
creases to 9 atom % at the eutectoid temperature (727°). The solu-
bility of vanadium in the β-form at a temperature of 700°, as well
as in the α-form at a temperature of 600°, is 1.5 atom %. The solu-
bility of uranium in vanadium (δ-phase) is at its maximum at the
eutectic temperature and is 4 atom % or 15% uranium by weight.

Sufficient information has recently become known to permit the

construction of a phase diagram for a vanadium-plutonium system [49], in a simple eutectic form (Fig. 18). The eutectic point occurs at 2.3 atom % vanadium at a temperature of 625°. The addition of vanadium has no effect on the polymorphic transitions of plutonium.

Fig. 17. Phase diagram of a vanadium-uranium system (black dots indicate points determined experimentally). 1) U, % by weight; 2) U, atom %.

Fig. 18. Phase diagram of a vanadium-plutonium system. 1) Pu, % by weight; 2) Pu, atom %.

The reactions of vanadium with the elements of Group IV, Subgroup B — oxygen and sulfur and its analogues — lead to the formation of thoroughly studied compounds.

There are no data on the reactions of vanadium with polonium.

Because of its great practical importance, the phase diagram for the vanadium-oxygen system has been studied repeatedly and in detail. The work by Pearson [50] makes a survey of previous works, and this work was devoted chiefly to the study of the vanadium oxides — VO, $V_2O_3$, $VO_2$, and $V_2O_5$ — their crystal structure and the conditions for and limits of their existence. The researchers A. Seybolt and H. Samison [51] discovered a high-temperature polymorphic

transformation of vanadium at a temperature of $1500^{\circ}$. This was shown on the phase diagram for a V-VO system proposed by the authors (Fig. 19a).

Oxygen dissolves in the α-form of vanadium in quantities up to 3.2 atom % and in the high-temperature γ-form in quantities up to 35-40 atom %. A more recent work [52] denies the existence of a high-temperature form of vanadium and gives a different phase diagram for the V-VO system (Fig. 19b). The alloys were produced from vanadium containing a total of 0.13% impurities, produced by the calcium-thermal method, and chemically pure vanadium pentoxide in electric arc furnaces. X-ray analysis, microstructural analysis, and measurements of electrical resistance as a function of temperature have been used to conduct this research. It was found that the limit of solubility of oxygen in α-vanadium at temperatures

Fig. 19. Phase diagram of a V-VO system. a) After Seybolt and Samsion; b) after Rostoker; 1) O, atom %; 2) $O_2$, atom %; 3) $O_2$. % by weight; 4) single phase; 5) two-phase; 6) three-phase; 7) thermal analysis.

below $900^{\circ}$ was between 0.27 and 0.98 atom %. At a temperature of

$1600^\circ$, the maximum solubility was approximately 3.9 atom %. X-ray analysis has shown that a β-phase region having a body-centered tetragonal lattice structure exists at room temperature when the oxygen content lies between 8 and 40 atom %. The authors consider this phase to be stable at high temperatures in a vanadium-oxygen system and believe it to be a low-temperature allotropic form of vanadium. The boundary of the phase α + β/β starts at 14.5 atom % oxygen at a temperature of $900^\circ$ to 22.1 atom % oxygen at a temperature of $1800^\circ$.

At temperatures lower than $1100^\circ$, a δ-phase whose crystal structure is not clear is formed by a peritectic reaction between the β-phase and the VO.

Between 41 and 56 atom % oxygen, there occurs a region of homogeneity for the compound VO, which has an NaCl-type structure with the lattice constant a = 4.08 kx.

In addition to studying the transition to the solid state, the authors of reference [48] investigated a fusibility diagram which showed a minimum at 30.2 atom % oxygen, corresponding to the minimum on the fusibility diagram compiled from the data of Seybolt and Samison. At the minimum temperature the β-phase solidifies rather than the γ-phase, as Seybolt and Samison had supposed. In the region 0-50 atom % oxygen, the fusibility diagram has two peritectic horizontals on both sides of the minimum. at temperatures which makes it possible to achieve the following reactions:

$$L + \alpha \rightleftarrows \beta \,(1850^\circ) \quad \text{and} \quad L + VO \rightleftarrows \beta \,(1690^\circ).$$
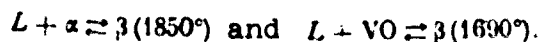
To confirm the hypothesis of a low-temperature allotropic form of vanadium, the authors of reference [52] measured the electrical resistance of a thin vanadium wire as a function of temperature in a vessel containing dry ice and acetone. The curve obtained (Fig. 20)

shows the change in electrical resistance (break) between -33 and
-25°.

Oxygen serves to stabilize the β-form. In a vanadium-oxygen system, this form has a substantial area of homogeneity.

The vanadium-sulfur system has been studied by means of a tensiometer, and by X-ray analysis [53]. The α-phase, VS, occurs in eutectic equilibrium with vanadium at a temperature of 1312° and has a structure of the nickel arsenide type;

Fig. 20. Change in electrical resistance of vanadium wire in temperature range -33 to -25°. 1) Resistance, ohms.

the β-phase, $V_2S_3$, which has an asymmetric lattice structure, falls between $VS_{1.17}$-$VS_{1.53}$. $VS_4$ is stable in the presence of sulfur at temperatures up to 400°. Reference [53] contains a repudiation of the existence of the previously discovered sulfide $V_2S_5$. The phase diagrams for a vanadium-selenium system and a vanadium-sulfur system are similar [50].

The following phases in the vanadium-selenium system were established in Reference [54] by X-ray analysis: VSe isomorphic to NiAs; $V_2Se_3$, which has a hexagonal lattice structure with slight symmetry; and $VSe_2$, isomorphic to $CdI_2$. Of the vanadium tellurides, VTe is already known and is isomorphic to NiAs [55].

Reactions with Elements of Group VII

No phase diagram has been constructed for systems containing vanadium and the metals of Group VII. However, sufficiently complete data is available on the reactions of vanadium with manganese and rhenium.

The formation of saturated solid solutions of vanadium in manganese is impossible because of the nonisomorphic crystal structures of the components and the existence of several polymorphic forms of manganese. However, in accordance with the rather small difference in the atomic diameters of the components, manganese is quite soluble in vanadium. No limit of solubility has yet been found for an alloy containing 14.2 atom % manganese at a temperature of 900° [3].

The alloy contains equal numbers of vanadium and manganese atoms, has a body-centered cubic crystal structure, and is considered as a metallic compound of vanadium and manganese with the composition VMn [56].

A σ-phase is formed in alloys rich in manganese with a region of homogeneity lying between 13.4 and 24.5 atom % vanadium at a temperature of 1000° [57].

There is an indication in the literature of the existence of the compound $Mn_2V$ (33.3 atom % vanadium) with a melting point of approximately 1370°. The $Mn_2V$ alloy, cast and annealed at temperatures of 1300° and 1200°, has a body-centered cubic crystal structure; the alloy annealed at temperatures of 1000, 800, and 600° is a mixture of two phases, one of which has a body-centered cubic crystal structure and the other a σ-phase structure [23].

Vanadium and rhenium differ only slightly in atomic diameter and this favors the formation of a considerable range of solid solutions between them. According to the data in reference [58], a solid solution of rhenium in vanadium contains up to 38 atom % rhenium and a solid solution of vanadium in rhenium contains up to 40 atom % vanadium. In the region of 40-66 atom % vanadium, no metallic compounds have been discovered.

X-ray studies have been carried out on alloys tempered at a temperature of 1200° after being subjected to homogenization annealing at the same temperature for three to five days.

There are no data on the reaction of vanadium with technetium. With the halogens, vanadium forms halogenides of the type $VH_2$, $VH_3$, and $VH_4$. Chlorides and iodides are of great importance as raw materials in the technology of the extraction of pure vanadium. Consideration of similar compounds is not within the scope of this work.

### Reactions with Elements of Group VIII

Vanadium should react with all elements of Group VIII by forming solid solutions and compounds with bonds of a metallic nature. For the nine elements in Group VIII, phase diagrams have been constructed only for iron [44, 59, 60], cobalt [61], nickel [3, 57, 62], and palladium [63].

The reaction of vanadium with iron is characterized by the formation of a continuous series of solid solutions, in accordance with the general conditions for the formation of saturated solid solutions between metals.

Fig. 21. Phase diagram of an iron-vanadium system. 1) V, atom %; 2) V, % by weight; 3) magnetic transition.

Figure 21 is a phase diagram for an iron-vanadium system as given in the handbook by Hansen [23]. With the cooling of an α-solid solution, a metallic compound corresponding to the formula FeV is formed at a temperature of 1230° [60].

By determining the distance between the lines on Debye crystallograms for various alloy compositions, it has been shown that the compound FeV is soluble both in iron and in vanadium. The region of homogeneity for this compound ($\sigma$-phase) lies between 37 and 57 atom % vanadium [40]. On examination of composition hardness and composition specific electrical resistance diagrams for alloys annealed at a temperature of $900^\circ$ for 70 hours, singular minima were discovered at 25 atom % vanadium, corresponding to the compound $Fe_3V$, and at 50 atom % vanadium corresponding to the compound FeV [64, 65]. A double iron-vanadium system has a closed region encompassing a phase-centered $\gamma$-solid solution whose upper limit lies at 1.2 atom % vanadium.

Certain data in the literature indicates the complexity of the phase transitions associated with the formation of a $\sigma$-phase. Reference [66] deals with the formation of a metastable ordered phase with a structure of the CsCl type at a temperature of $600^\circ$ in an equiatomic alloy which is tempered while an $\alpha$-solid. This phase precedes the formation of a stable $\sigma$-phase.

The research described in reference [67] shows that a second ferromagnetic phase is formed in an iron alloy containing 47% vanadium under certain heat-treating conditions. In this case, high-temperature annealing at a temperature of $1350^\circ$ for 60 hours with subsequent quenching in an alkali is of decisive importance. The change in magnetic properties and microstructure discloses the formation of a second magnetic phase $\sigma'$, whose quantity in alloys annealed at various temperatures increases until a temperature of $975^\circ$ is achieved.

Reference [68] studies the structure of iron alloys containing 28.5, 43, 49.5, and 74 atom % vanadium after heating at various

temperatures from 600° to 1400° with subsequent quenching in water. In accordance with X-ray research and the microstructure data on the alloys, all alloys consist of a mixture of the two phases α + β in the temperature region 1400-1150°. In the opinion of the authors, the second phase — the cubic, face-centered β-phase — is the equilibrium phase and the quantity of this phase increases with an increase in vanadium content. At a temperature of 800°, an alloy containing 28.5% vanadium consists of a single α-phase, while alloys containing 43, 49.5, and 74% vanadium consist of two phases — α and σ. At a temperature of 600°, an alloy containing 49.5 % vanadium exhibits no α phase crystals; the structure is purely σ-phase.

Thus, the authors of reference [68] consider the iron-vanadium system to have a more complex phase transformation in the region of 28.5 to 74 atom % vanadium when the temperature is reduced from 1400 to 600° than might be concluded from the phase diagrams in the literature.

Fig. 22. Phase diagram of a vanadium-cobalt system.
1) Co, atom %.

Cobalt and nickel, the analogues of iron, differ more widely in atomic diameter from vanadium than does the former and are not isomorphic to it in crystal structure. This explains the limited solubility of cobalt and nickel in vanadium.

According to data given in the literature [61], the solubility

of cobalt in vanadium is 20 atom % at high temperatures and 5% at room temperature.

The phase diagram for a vanadium-cobalt system [1, 6], constructed in accordance with data on hardness, and thermal, microstructural, and X-ray diffraction analyses, is shown in Fig. 22. At the temperature of the eutectic, $1248^{\circ}$, $\gamma$ and $\beta$-phases are found in equilibrium with the melt. A $\sigma$-phase is formed at a temperature of $1420^{\circ}$ by a peritectic reaction between the melt and the vanadium solid solution. The region of homogeneity for the $\sigma$-phase, a solid solution based on the compound CoV, lies between 38.5 and 59.5 atom % vanadium [57]. In an alloy containing 70.7 atom % vanadium, a eutectic reaction occurs at a temperature of 1100 to $1150^{\circ}$ between the $\alpha$ and $\beta$-phases with the formation of the metallic compound $CoV_3$ which crystallizes into a structure of the $\beta$-tungsten type. A new ordered phase $(\gamma)$ is formed in the region of the cobalt solid solution at a temperature of $1070^{\circ}$ [69]. This phase is based on the compound $Co_3V$ and has a region of homogeneity between 19.1 and 26.09 atom % vanadium. There are two-phase regions $\gamma + \gamma'$ and $\gamma' + \sigma$ on both sides of this homogeneous region. The $\gamma' + \sigma$ phase is formed by a eutectic reaction at a temperature of $1040^{\circ}$. The well regulated phase exhibits weak superstructural lines on an X-ray diffraction diagram.

According to the data in reference [3] the solubility of nickel in vanadium is 6 to 9 atom %. The phase diagram of a nickel-vanadium system [62] containing up to 60% vanadium is shown in Fig. 23. At the eutectic temperature an $\alpha$-solid solution of vanadium and nickel and a $\sigma$-phase are found in equilibrium at the eutectic temperature. The $\sigma'$-phase has a substantial region of homogeneity extending from 55 to 74 atom % vanadium and, at a temperature of $76^{\circ}$,

undergoes the transformation $\sigma' \rightarrow \sigma$, the nature of which is not as yet known. The $\sigma$- and $\sigma'$-phases do not differ on the X-ray diffraction diagram. The boundaries $\alpha/\alpha + \sigma$ and $\alpha + \sigma'/\sigma$ have been established by X-ray diffraction analysis. At a temperature of $840^{\circ}$, the eutectoid decomposition $\alpha \rightleftarrows \delta + \sigma'$ occurs, while at $907^{\circ}$ the euctectoid decomposition $\alpha \rightleftarrows \theta + \delta$ occurs. The $\delta$-phase, which has a body-centered orthorhombic crystal structure, is a solid solution based on the compound $Ni_2V$ (30.27% vanadium by weight). The $\theta$-phase, which has a tetragonal lattice structure of the $TiAl_3$ type, is a solid solution based on the compound $Ni_3V$ formed at a temperature of $1045^{\circ}$.

There are indications [3, 70] of the formation of the compound $NiV_3$ (72.25% vanadium by weight) with the structure of $\beta$-W in regions rich in vanadium by a peritectic reaction at a temperature of $1380^{\circ}$.

Only unsaturated solid solutions in metallic compounds can be formed between vanadium and the elements of the platinum group because the crystal structures of these elements are not isomorphic to vanadium. The alloys of vanadium with palladium are the most fully studied [58, 63], but alloys of vanadium with ruthenium, rhodium, and platinum have been partially investigated [58]. There is no information in the literature on the reactions of vanadium with osmium and iridium.

A vanadium-palladium phase diagram is of the eutectic type (Fig. 45). At the eutectic temperature of $1340^{\circ}$, the $\alpha$-solid solution of palladium in vanadium, at this temperature containing up to 37.5 atom % palladium, is in equilibrium with $\gamma$-solid solution of vanadium in palladium. At a temperature of $840^{\circ}$, the compound $PdV_3$, which has the structure of $\beta$-W with a = 4.80 kx and iso-

morphic to $CoV_3$ and $NiV_3$, is formed by a peritectic reaction. This compound has a wide region of homogeneity and is not plastic. Two metallic compounds $Pd_3V$ and $Pd_2V$ are formed in the region of the $\gamma$-solid solution during its stabilization, at temperatures of 815 and $905^\circ$, respectively. These compounds have a face-centered tetragonal lattice structure with the lattice constants $a = 3.84$ kx, $c = 3.87$ kx, $c/a = 1.007$ for $Pd_3V$ which is isomorphic to $Ni_3V$ and $a = 3.88_2$ kx, $c = 3.72_9$ kx, and $c/a = 0.962$ for $Pd_2V$. The eutectic reaction $\gamma \leftrightarrows Pd_3V + Pd_2V$ occurs at a temperature of $720^\circ$ and 28 atom % vanadium. At room temperature, the field of the $\gamma$-phase exists not only at vanadium contents up to 21 atom %, but also between 44 and 50% vanadium.

At a temperature of $500^\circ$, the solubility of palladium in vanadium is 15 atom %. There is no definite data on the solubility of ruthenium in vanadium. Alloys containing 36, 50, 71, and 82 atom %

Fig. 23. Phase diagram of a nickel-vanadium system. 1) V, % by weight; 2) V, atom %.

ruthenium have been studied as described in reference [58] by X-ray diffraction after tempering at a temperature of $1200^\circ$. The

alloy containing 36 atom % ruthenium has a cubic lattice structure of the CsCl type with lattice constants very similar to those of a solid solution based on vanadium. A phase having a tetragonal lattice structure was found in the alloy containing 50 atom % ruthenium. According to reference [58] a solid solution of vanadium in ruthenium contains less than 18 atom % vanadium.

Fig. 24. Phase diagram of a vanadium-palladium system.
1) Pd, atom %.

Reference [54] describes research on alloys containing 25, 42, 50, and 60 atom % rhodium which was tempered at a temperature of $1200^{\circ}$. The compound $V_3Rh$ (42.24% rhodium by weight) with a crystal lattice structure of the $\beta$-W type has been detected. A second compound with a tightly packed hexagonal lattice structure was found in the alloy containing 60 atom % rhodium.

The limit of solubility of platinum in vanadium [37] is 8 atom % or 25% platinum by weight, while the solubility of vanadium in platinum is 40 atom % [58]. The compound $V_3Pt$ (43.91% vanadium by weight), isomorphic to $V_3Pd$, has been discovered in the vanadium-platinum system. It is only possible for one compound to exist between a rich platinum solid solution and $V_3Pt$ [58].

The nature of the reactions of vanadium with elements of the periodic system here considered and the basic properties of vanadium are set forth in Tables 3 and 4.

Tables 3 and 4 are a portion of the general table of metallo-chemical properties of the elements of the periodic system of D.I.

Mendeleyev, as suggested by one of the authors of this article [71].

TABLE 3

Basic Properties of Vanadium and Their Reactions with the Elements of the Periodic System.

| 1 Порядковый номер элемента — 23 | 2 Атомный вес — 50,95 | 3 Атомный радиус — 1.34 Å | 4 Ионные радиусы, Å 5⁺—0,4 3⁺—0,74 |
|---|---|---|---|
| 5 Решетка — кубическая, объемно-центрированная | 6 Распространенность в земной коре, вес. % 1,5·10⁻² | 7 Электронное строение —3d² —4s² | 8 Потенциал ионизации 68,64 в |

1) Atomic number of element - 23; 2) atomic weight - 50.95; 3) atomic radius -1.34 A; 4) ionic radii, A; $5^+$ - 0.4, $3^+$ -0.74; 5) lattice structure - body-centered cubic; 6) occurrence in earth's crust, percent by weight, $1.5 \cdot 10^{-2}$; 7) electron configuration; $3 d^2$, $4s^2$; 8) ionization potential, 68.64 v.

TABLE 4

Reactions of Vanadium with Elements of the Periodic System

| 1 Непрерывные твердые растворы | 2 Органические твердые растворы | 3 Металлические соединения |
|---|---|---|
| β — Ti; Cr; α — Fe; Nb; Mo; Ta | Be; B; N; O; Al; Si; α — Ti; Mn; Co; Ni; Cu; Ge; Zr; Ru; Rh; Sn; W; Re; Pt; Au; U; Pd | Be; Al; Mn; Ca; Ni; Ge; Zr; Rh; Sn; Sb; Ht; Ru; Pd; Pt и 4 металлоиды III—IV групп |

1) Saturated solid solution; 2) unsaturated solid solution; 3) metallic compounds; 4) metalloids of Groups III-IV.

## CONCLUSIONS

1. The extraction of vanadium in pure form has opened broad prospects for the practical use of vanadium and its alloys.

The existence of very pure vanadium has forced us to reconsider the previously used phase diagrams which were constructed for technically pure vanadium (95-96% vanadium) and this serves as a basis for the broad development of work on the metallochemistry of vanadium.

2. In work published in 1954 [3] twenty-one double systems of

vanadium with other elements were studied. Analysis of this work and other works for the purpose of determining general quantitative relationships for the formation of metallic solid solutions and compounds has shown that these rules extend to the reactions of vanadium with other elements of the periodic system.

3. The formation of solid solutions or the absence of such solutions in double systems containing vanadium is a function of the similarity or difference in the chemical properties of the elements, as determined from the periodic law of D.I. Mendeleyev, and the magnitudes of their atomic diameters.

4. The metal-analogues of vanadium — niobium and tantalum, and the elements of groups IV and VI which are in proximity to vanadium — as well as iron, which differ least from vanadium with respect to atomic diameters and isomorphic crystal lattices, are capable of producing saturated solid solutions with vanadium.

5. Elements differing from vanadium in physicochemical properties, the elements of groups I and II (with the exception of the alkali and alkali-earth elements) and the elements of groups III, VII, and VIII give unsaturated solid solutions and metallic compounds with vanadium.

6. Such metalloids as H, P, C, Si, N, and O, which are of small atomic diameter, form only highly unsaturated solid solutions of the interstitial or substitution type with vanadium. To a great extent, they tend to form compounds of the following types: borides, carbides, silicides, nitrides, and oxides of vanadium.

7. The establishment of the general nature of the reactions of the elements of the periodic system with vanadium, from the point of view of the formation of metallic solutions and compounds, facilitate the systematization of phase diagrams for two-component systems

based on vanadium, the majority of which have still not been studied, and the general representation of more complex multicomponent equilibrium systems based on vanadium.

## REFERENCES

1. I.I. Kornilov, Izv. AN SSSR, OKhN, [Bulletin of the Academy of Sciences USSR, Department of Chemical Sciences], 1957, No. 4.

2. I.I. Kornilov, Zh. neorganich, khim. [Journal of Inorganic Chemistry], 1958, No. 2, p. 320.

3. W. Rostoker, A. Yamamoto. Trans. ASM, 1954, 46, 1130.

4. Yum-Rozeri. Struktura metallov i splavov [The Structure of Metals and Alloys], Izd-vo GONTI [State United Publishing House of Science and Technology], 1938.

5. H.V. Ageyev, Izv. sektora fiz.-khim. analiza [Bulletin of the Department of Physicochemical Analysis], 1938, No. 8, p. 175.

6. I.I. Kornilov, Zheleznyye splavy [Iron Alloys], Vol. II, Moscow-Leningrad, izd-vo AN SSSR [Publishing House of the Academy of Sciences USSR], 1951.

7. I.I. Kornilov, Izv. AN SSSR, OKhN, 1950, No. 5.

8. I.I. Kornilov, Izv. AN SSSR, OKhN, 1953, No. 5.

9. I.I. Kornilov, Izv. AN SSSR, OKhN, 1954, No. 3.

10. I.I. Kornilov, Dokl. AN SSSR [Proceedings of the Academy of Sciences USSR], 1950, 72, No. 3.

11. G.A. Meyerson, G.A. Kats, A.V. Khokhlova, Zh. neorganich. khim., 1940, No. 13, pp. 1770-1776.

12. H. Hagg, Z. phisikal Chem. [Journal of Physical Chemistry], 1931, 11, 444.

13. Yadernyye reaktory [Nuclear Reactors], Vol. III, Mat. dlya yadernykh reaktorov [Mathematics for Nuclear Reactors], izd-vo inostr. lit. [Publishing House for Foreign Literature], 1956.

14. D. Summers-Smith, et al. J. Inst. Metals, 1954-1955, 83, 189.

15. P. Schwarzkopf, F. Glaser, Z. Metallkunde [Journal of Physical Metallurgy], 1958, 44, 353,358.

16. D. Nowotny, F. Benesovsky, R. Kieffer, Z. Metallkunde, 1959, 50, 258.

17. D. Moskowitz. Trans. AJME, 1956, 206, 1526.

18. O. Carlson et al. Trans. ASM, 1955, 47.

19. H. Adenstedt et al. Trans. ASM, 1952, 44, 990.

20. P. Pietrokowsky, P. Duwez. J. Metals, 1952, 81, 73.

21. E. Brotzen, E. Harmond, A. Troiano. J. Metals, 1955, 7, No. 2, 413-419.

22. K. Lohberg, H. Westphal. Z. Metalljunde, 1958, 49, No. 9, 449-455.

23. M. Hansen. Constitution of binary alloys, 1958.

24. H. Giebelhausen, Z. anorg. allg. Chem. [Journal of Inorganic and General Chemistry], 1915, 91, 6, 254.

25. N. Schonberg. Acta Chem. Scand., 1954, 8, 624-626.

26. G.V. Samsonov, Ya.S. Umanskiy, Tverdyye soyedineniya tugoplavkikh metallov [Solid Compounds of High-Melting Metals], Metallurgizdat [State Scientific and Technical Publishing House for Literature on Ferrous and Nonferrous Metallurgy], 1957.

27. M.A. Gurevich, B.F. Ormond, Dokl. AN SSSR, 1954, 96, p. 1165.

28. A. Osawa. M. Oya. Sci. Repts Tohoku Univ., 1930, 19, 95.

29. H. Nowotny, R. Kieffer, F. Benesovsky, E. Laube, Monatsh. Chem. [Chemical Monthly], 1957, 88, 3, 339-341.

30. E. Parthe, N. Nowotny, H. Schmid. Monatsh. Chem., 1955, 86, 3, 385-396.

31. R. Kieffer, F. Benesovsky, H. Schmid. Z. Metallkunde, 1956, 47, 4, 247.

32. H. Nowotny, et al. Montash. Chem. 1954, 85, 1, 242.

33. R. Kleffer, P. Benesovsky, Symposium on powder metallurgy, Special Report, No. 58, 1958.

34. Ye.I. Gladyshevskiy, Yu.B. Kuz'ma, Dokl. AN UkSSR [Papers presented to the Academy of Sciences, Ukrainian SSR], 1958, 11, pp. 1208-1211.

35. N. Wallbaum, Naturwiss [Natural Science], 1944, 32, 76.

36. W. Koster, K. Haug, Z. Metallk. [Journal of Physical Metallurgy], 1957, 48, 327.

37. S. Geller, et al.J. Amer. Chem. Soc., 1954, 77, 6, 1504.

38. H. Wilhelm, et al. Trans. AJME, 1954, 200, 915.

39. I.I. Kornilov, Usp. Khim [Progress in Chemistry], 1952, Issue 9, p. 1045.

40. H. Hahn. Z. anorg. Chem., 1949, 258, 58.

41. Rukovodstvo po preparativnoy neorganicheskoy khimii [Handbook of Preparative Inorganic Chemistry], edited by G. Bauer, izd-vo inostr. lit., 1956.

42. M. Zumbusch, W. Biltz. Z. anorg. Chem., 1942, 249, 1.

43. H. Nowotny, R. Funk. J. Pesl. Monatsh. Chem., 1951, 82, 519.

44. H. Marden, D. Duwez. Trans. ASM, 1952, 44.

45. W. Pearson, et al., Nature, 1951, 167, 20.

46. E Pipitz, R. Kieffer. Z. Metallkunde, 1955, 46, 187.

47. V.V. Baron, Yu.V. Yefimov, Ye.M. Savitskiy, Izv AN SSSR, OTN [Bulletin of the Academy of Sciences USSR, Department of Technical Sciences], 1958, No. 4, pp. 36-40.

48. H. Saller, F. Rough. Trans. ASME, 1953, 197, 545.

49. S.G. Konobeyevskiy, Sessiya Akademii nauk SSSR po mirnomy ispol'zovaniyu atomnoy energii 1-5 iyunya 1958 [Meeting of the Academy of Sciences USSR on the Peaceful Uses of Atomic Energy, 1-5 June

1958], Zasedaniye otdeleniya khimicheskikh nauk [Meeting of the Department of Chemical Sciences], Izd-vo AN SSSR, p. 367, 1955.

50. W. Pearson, J. Iron and Steel Inst., 1950, 164, 149.

51. W. Rostoker, A. Yamamoto, Trans. ASM, 1955, 47, 1002.

52. A. Seybolt, H. Samsion. J. Metals, 1953, 5 (2), 2.

53. W. Biltz. A. Kocher. Z. anorg. Chem., 1939, 241, 224.

54. H. Hoschek, W. Klemm. Z. anorg. Chem., 1939, 242, 49-62.

55. P. Ehrlich. Z. anorg. Chem., 1949, 260, 1-18.

56. W. Pearson, et al., Nature, 1951, 167, 20.

57. P. Greenfield. P. Beck. Trans. AJME, 1954, 200, 253.

58. P. Greenfield, P. Beck. Trans. AJME, 1956, 206, 265-276.

59. R. Vogel, G. Tamman. Z. anorg. allg. Chem., 1908, 58, 79.

60. F. Wever, W. Jellinhaus, Mitt. Kais. Wilh. Inst. Eisen-forschg [Bulletin of the Kaiser Wilhelm Institute for Iron Research], 1930, 12, 1377.

61. W. Koster. H. Schmid. Z. Metallkunde. 1955, 46, 195.

62. W. Pearson. W. Hume-Rothery. J. Inst. Metals, 1952, 80, 641.

63. W. Koster, W. Haehe. Z. Metallkunde, 1958, 49, 12, 647.

64. N.M. Matveyeva, Fazovyye prevrashcheniya v troynoy sisteme zhelezo-khrom-vanadiy [Phase Transformations in a Ternary Iron-Chromium-Vanadium System], Author's Abstract of Dissertation, Moscow, 1955.

65. I.I. Kornilov, V.S. Mikheyev. Dokl. AN SSSR, 1955, 104, No. 1. pp. 88-90.

66. P. Greenfield, P. Beck. Trans. AJME, 1956, 206, 148.

67. M.I. Zakharova, P.N. Stetsenko, Vestn. MGU, seriya khim. [Herald of the Moscow State University, Chemical Series], 1957, No. 5, pp. 53-61.

68. M.I. Zakharova, et al., Dokl. AN SSSR, 1958, 119, No. 3,

pp. 489-500.

69. P. Duwez. Trans. AJME, 1951, 191.

70. W. Rostoker. J. Inst. of Metals, 1952, 80, 698.

71. I.I. Kornilov, Metallokhimicheskiye svoystva elementov periodicheskoy sistemy D.I. Mendeleyeva (Referaty dokladov) [The Metallochemical Properties of the Elements of the Periodic System of D.I. Mendeleyev (Abstracted Papers)], Izd-vo AN SSSR, 1958.

[List of Transliterated Symbols]

Manu-
script
Page
No.

60        пл= pl = plavleniye = melting

# RESEARCH ON VANADIUM-COPPER-CARBON AND VANADIUM-COPPER-ALUMINUM ALLOYS

By Ye.M. Savitskiy, V.V. Baron, and Yu.V. Yefimov

No phase diagram for the vanadium-copper system has as yet been published. There is information in the literature on investigations of the copper angle of this phase diagram [1-5]. The alloys at the vanadium angle have been investigated by Rostoker and Yamamoto [6, 7] who established only that copper enters into a vanadium-based solid solution in quantities of approximately 7.5-10% by weight. There are no data in the literature on the physical and mechanical properties of these alloys.

The work which we will describe here was undertaken for the purpose of investigating the structure and properties (microstructure, hardness, microhardness, plasticity, and strength) of the alloys at the vanadium angle of the vanadium-copper-carbon and vanadium-copper-aluminum systems.

Preparation of alloys. Vanadium produced by the aluminothermal and carbothermal methods (Table 1) and Type MO electrolytic copper were used as the initial materials for producing the alloys. Smelting was carried out in an arc furnace with a nonconsumable tungsten electrode, at a pressure of 0.5 atm in a helium atmosphere. Before the experimental alloys were smelted, a titanium specimen was melted as a getter to purify the helium. After being smelted four times, the ingot being turned in the sole compartments in order to

TABLE 1

Chemical Composition of Initial Vanadium, in Percent (%) by Weight

| 1 Материал | V | C | O | N | Al | Fe | Si | Mn |
|---|---|---|---|---|---|---|---|---|
| 2 Алюминотермический ванадий | 96,5 | 0,05 | 0,8 | 0,27 | 1,5 | 0,15 | 0,3 | 0,1 |
| 3 Карботермический ванадий | 98,0 | 1,6 | 0,3 | 0,02 | Металлические примеси в сумме не больше 0,2 % 4 | | | |

1) Material; 2) aluminothermal vanadium; 3) carbothermal vanadium;
4) metallic admixtures in amounts not exceeding 0.2%.

ensure uniform composition, the melts are poured in quantities of approximately 50 g into a square column (h = 50-60 mm),(10 X 10), using a specially designed sole fabricated in the Rare Metal Alloys Laboratory of the Institute of Metallurgy of the Academy of Sciences USSR. The specimens were cast in iron molds. The aluminum-containing alloys were prepared by adding copper to aluminothermal vanadium and those containing carbon were prepared by adding copper to carbothermal vanadium.

The copper, carbon, and aluminum contents of the alloys obtained were determined by chemical analysis (Table 2). After their microstructure was studied and their hardness measured, the cast alloys were subjected to homogenization annealing in evacuated double quartz ampules for 100 hours at a temperature of $1000^{\circ}$ and then cooled to room temperature with the furnace (24 hours). To make the specimens, the ingots were cut under small but constant pressure with silicon carbide stones. This cutting material was used because of its great hardness and poor workability. The microsections were prepared by mechanical polishing with abrasive papers of different grades and by wet grinding with chromium oxide cloth. The microsections were pickled in a mixture of hydrofluoric (95%) and nitric (5%) acids.

The hardness $(H_k)$ is determined by the application of a carboloy

# TABLE 2

Composition of V-Cu-Al and V-Cu-C Alloys and Thermal Analysis Data

| 1) Сплав | 2) Химический анализ, вес. % | | | 3) Термический анализ при температуре, °С | | |
|---|---|---|---|---|---|---|
| | Cu | Al | C | 4) Плавление медной фазы | 5) солидус | 6) ликвидус |
| 1 | 0,00 | 1,61 | 0,05 | — | 1795 | — |
| 2 | 0,25 | — | — | — | — | — |
| 3 | 0,4 | — | — | — | 1745 | — |
| 4 | 0,8 | 1,64 | — | — | 1720 | 1795 |
| 5 | 3,12 | — | — | — | 1635 | 1780 |
| 6 | 5,92 | — | 0,02 | — | 1580 | 1775 |
| 7 | 6,70 | — | — | — | 1570 | — |
| 8 | 7,35 | 1,37 | — | — | — | — |
| 9 | 8,01 | — | — | — | — | — |
| 10 | 8,67 | — | — | — | 1540 | 1710 |
| 11 | 11,51 | 1,31 | — | 1130 | 1530 | 1725 |
| 12 | 14,36 | — | 0,02 | 1120 | 1530 | 1610 |
| 13 | 17,58 | — | — | 1120 | 1530 | — |
| 14 | 20,99 | — | — | 1120 | 1530 | — |
| 15 | 0,00 | — | 1,61 | — | 1820 | — |
| 16 | 0,2 | — | — | — | 1750 | — |
| 17 | 0,4 | — | — | — | 1660 | 1820 |
| 18 | 0,54 | — | 1,47 | — | 1690 | — |
| 19 | 1,08 | — | 1,37 | — | 1600 | 1820 |
| 20 | 2,97 | — | 1,65 | — | 1585 | 1800 |
| 21 | 3,73 | — | 1,52 | — | 1575 | 1800 |
| 22 | 9,10 | — | 1,39 | 1110 | 1575 | 1650 |
| 23 | 14,23 | — | — | 1110 | 1575 | — |
| 24 | 20,58 | — | — | 1110 | — | — |

1) Alloy; 2) chemical analysis, in % by weight; 3) thermal analysis at temperature, °C; 4) melting of copper phase; 5) solidus; 6) liquidus.

point for 30 seconds under a load of 50 kg. The microhardness of the alloys was determined with a PMT-3 instrument at a load of 100 g. The strength and plasticity of the alloys were determined by compressing 4 x 4 x 6 mm specimens in a Gagarin press.

Microstructure of the alloys. Microscopic analysis of the cast V-Cu-Al alloys showed the presence of stratification regions in the system. In alloys containing more than 14.4% Cu by weight, a non-uniform distribution of copper-phase inclusions is noted along the ingot, this causing considerable scattering of data in chemical analysis, and a very thin second layer of the copper phase (an alloy containing 17.1% by weight Cu) appears at first in the lower sections of the ingot. When the copper content in the alloy is increased, the thickness of the copper-phase layer increases and this indicates

Fig. 1. Change in microstructure of V-Cu-Al alloy containing 21.0% Cu by weight, along the vertical cross section of the ingot (100X).

the immiscibility in the liquid and solid states. Moving upward along the ingot, from the copper-phase layer, the number of second phase inclusions gradually decreases. White, oval dispersed inclusions of the vanadium phase may also be seen in the copper-phase layer (Fig. 1). No stratification was observed in cast alloys containing less than 14.4% Cu by weight.

Alloys containing from 8.0 to 14.4% Cu by weight were two-phase in the cast state with uniform distribution of the red inclusions characteristic of copper along the ingot. The remaining alloys with lower copper contents were single-phase. Homogenization annealing had no material effect on the structure of the alloys.

Thus, microstructural analysis of V-Cu-Al alloys has made it possible to establish the immiscibility of the liquid and solid states, whose boundary on the vanadium side occurs at 16% Cu by weight. At room temperature, the solubility of copper in the vanadium-based solid solution was approximately 7.5% by weight. When the copper content was increased, the second phase (the copper-based solid solution) increased in size. The inclusions of the second (lower-melting) phase were located principally along the grain bound-

aries of the vanadium solid solution. No indications of a eutectic
formed between the solid solution and the copper phase in these
alloys have been detected. Black inclusions of impure vanadium
which may easily be distinguished from the color of the copper phase
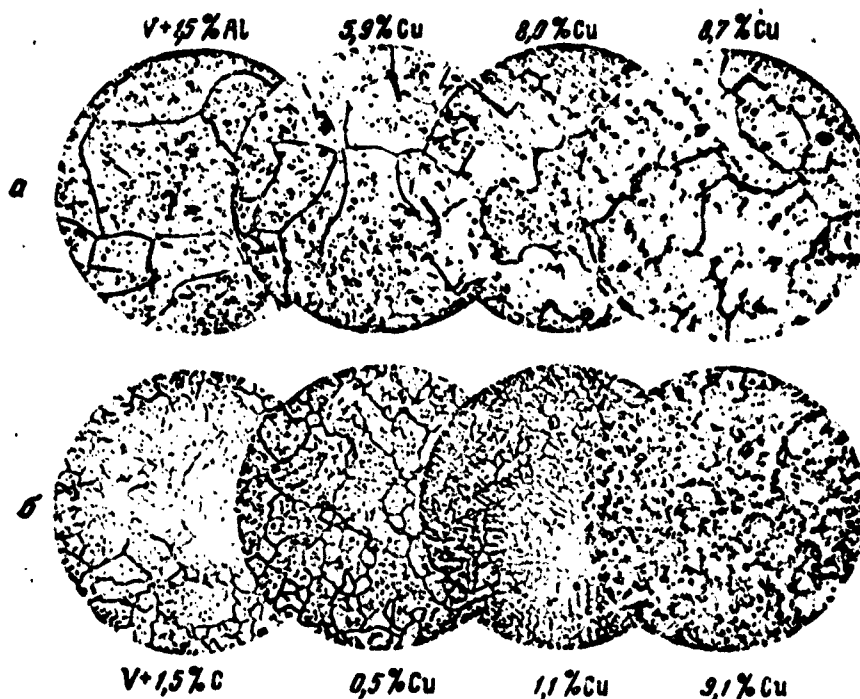by visual inspection were found in the microstructure of the annealed
alloys (Fig. 2a).



Fig. 2. Microstructure of annealed alloys (100X). a) V-Cu-Al
alloys; b) V-Cu-C alloys.

Microstructural phase analysis was used to determine the limit
of solubility of solid copper in the vanadium-based solid solution.
High-temperature forms of the alloys were produced by quenching in
water at temperatures of 600, 800, 1000, 1350, and 1500°.

Isothermic soaking (50 hours) at the first three temperatures
was carried out in evacuated quartz ampules and at temperatures of
1350 and 1500° was carried out in a special setup for high-tempera-
ture quenching. The specimens were heated by passing a current
through them for 1 hour with subsequent quenching in water. After

the heat treatment, the alloys were subjected to metallographic analysis.

Microstructural phase analysis showed that the solubility of copper in a solid solution of the vanadium-based V-Cu-Al alloys increases with temperature and reaches a maximum at $1530^\circ$ (9.5% Cu by weight).

Individual small inclusions of the second phase were seen in the microstructure of V-Cu-C alloys containing 1.1% Cu by weight (Fig. 2b). These inclusions increased in number as the copper content increased. At room temperature, the limit of solubility of copper in a solid solution of the vanadium-based V-Cu-C alloys containing 1.5% C by weight, is approximately 1% by weight.

It was established that stratification is present in alloys containing 14.0 and 20.6% Cu by weight. The boundary of the immiscibility region for these alloys lies at 11% Cu by weight.

Thus, the presence of carbon in vanadium-copper alloys decreases the solubility of the copper in the vanadium and broadens the region of their immiscibility.

Microstructural phase analysis of V-Cu-C alloys was carried out after quenching at temperatures of 1000, 1350, and $1500^\circ$.

The solubility of copper in a solid solution of the vanadium-based V-Cu-C alloys containing 1.5% C by weight increases with temperature and reaches a maximum at $1575^\circ$ (3.5% Cu by weight).

Thermal analysis. Thermal analysis was carried out by two methods. In the first of these, the solidus temperature was determined by an optical pyrometer, using the appearance of a drop of molten metal in a depression (depression diameter, 1 mm; depth, 3.5 mm) in a 4 x 4 x 5 mm specimen, this being carried out on a special device. The liquidus temperature was determined at the tem-

96

perature at which the specimen melted through at a previously weak-
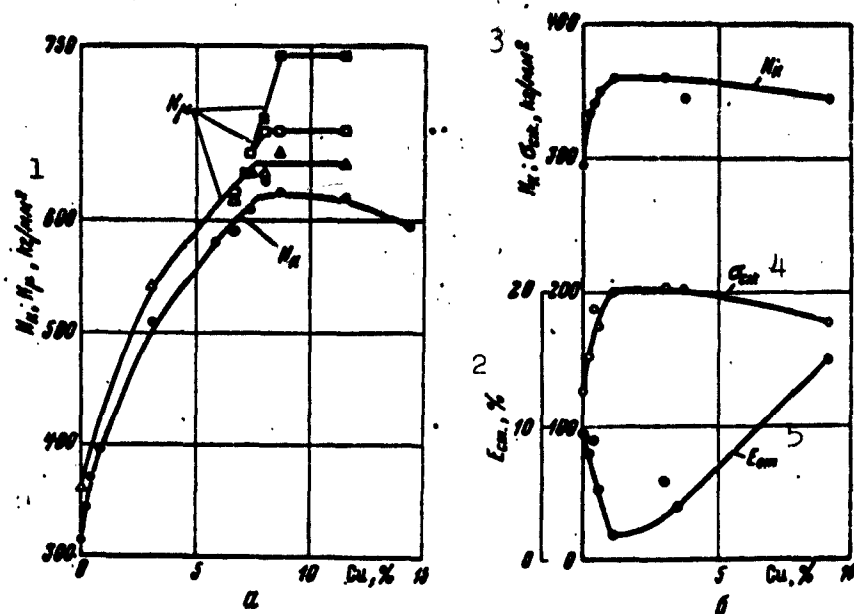ened point. The specimen was heated by passing a current through it
in a vacuum.



Fig. 3. Properties of alloys. a) V-Cu-Al alloy (1.5% Al
by weight); b) V-Cu-C alloy (1.5% C by weight). Experi-
mentally determined points: ● — $H_k$; O — $\sigma_{szh}$; Δ — $H_{mk}$,
annealing, quenching at $600°$; □ — the same, quenching at
$1000°$; ■ — the same, quenching at $1350°$. 1) $H_k$, $H_\mu$, kg/mm$^2$;
2) $E_{st}$, %; 3) $H_k$; $\sigma_{szh}$, kg/mm$^2$; 4) $\sigma_{szh}$; 5) $E_{st}$.

Differential microthermal analysis was used to substantiate
the results and increase their accuracy. In this method, the heating
curves of the alloys were recorded on a special device by a record-
ing pyrometer of the type designed by N.S. Kurnakov and by high-
temperature differential and ordinary Rh-Pt/Rh thermocouples. A
one gram sample of the alloy was fastened to the exposed junction
of the thermocouple. Heating was effected at a rate of 30 deg/min
by a tungsten heater. The change in temperature of each alloy was
recorded twice. In both methods, calibration was carried out at the
melting points of pure metals (Ag, Cu, Ni, Ti, Zr, Pd). The results
obtained by these two methods were in good agreement.

The introduction of copper reduces the melting point of vanadium. The point of intersection of the solidus curve with the monotectic horizontal ($1530^\circ$ for V-Cu-Al alloys) corresponds to the limit of solubility of copper in the vanadium-based solid solution (9.4% by weight). In alloys containing more than 8.7% Cu by weight, the melting point of the copper phase is fixed at $1120^\circ$ for all alloys. Thermal analysis of V-Cu-C alloys (Table 2) has shown that carbon increases the monotectic equilibrium temperature ($1575^\circ$).

Properties of the alloys. Annealed V-Cu-Al alloys, within the limits of the solid solution, undergo an increase in hardness ($H_k$) and microhardness ($H_{mk}$) when the carbon content is increased. In the transition to a two-phase region, the hardness remains constant over a certain concentration range and then slowly decreases in hardness when the amount of the softer second phase is increased. Measurements of the microhardness of quenched alloys completely confirm the results of microstructural analysis. When compressed, V-Cu-Al alloys, just as vanadium alone, undergo brittle fracture as a result of interstitial elements present as impurities (Fig. 3a).
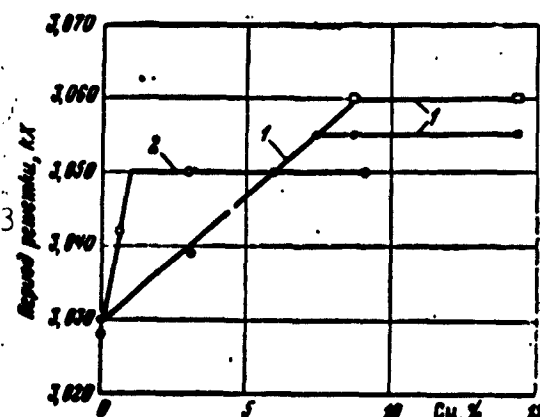
Fig. 4. Lattice constants of α-solid vanadium solution in alloys. 1) V-Cu-Al (1.5% Al); 2) V-Cu-C (1.5% C by weight); 3) lattice constant, kx; Experimentally determined points: ● — annealing; □ — quenching at $1000^\circ$; ○ — annealing.

The results of measuring the hardness $H_k$, the plasticity $E_{st}$, and the strength of annealed V-Cu-C alloys subjected to a compressive stress $\sigma_{szh}$ (Fig. 3b) indicate that a sharp increase in hardness and strength and a decrease in plasticity occur within the

solid solution. Inflection in the curves is observed with a Cu content of approximately 1% by weight in the alloys. When the copper content is further increased (up to 10% by weight), there is virtually no change in hardness, strength decreases, and plasticity increases, obviously as a result of an increase in the quantity of the plastic copper phase.

X-ray analysis. Powders made from the annealed and quenched (at 600 and 1000°) alloys were subjected to X-ray analysis. The X-ray exposures were made by copper radiation in an RKU camera with a filter. Calculation of the lattice constants showed that an increase in lattice constants occurred, up to the saturation point, when copper was dissolved in the vanadium-based solid solution of alloys V-Cu-Al (Fig. 4). The lattice constant of aluminothermal vanadium is a = 3.030 kx, that for the saturated, vanadium-based, annealed solid solution is a = 3.055 kx, and that for the solid solution quenched at 1000° is a = 3.060 kx. When the alloys are quenched at 600°, the lattice constant of the saturated solid solution is the same as that for the annealed alloy (within the error limits of the experiment). For alloys having a two-phase region (containing more than 9% Cu by weight), copper phase lines are observed, in addition to the vanadium solid solution lines (these denote a solid solution of vanadium in copper having a face-centered cubic lattice structure and a lattice constant a = 3.620 kx).

The lattice constant function for the α-solid solution of annealed V-Cu-C alloys is also shown in Fig. 4. The lattice constant of the α-solid solution of carbon in vanadium is a = 3.028 kx and that for the saturated copper of the α-solid solution is a = = 3.050 kx. According to X-ray data, the limit of solubility of copper in the vanadium-based solid solution of V-Cu-C alloys (1.5% C by weight) is also 1% Cu by weight.

Weak lines representing a second vanadium phase with a hexago-
nal lattice structure, apparently a γ-phase, were observed together
with the α-solid solution lines on the X-ray diffraction patterns
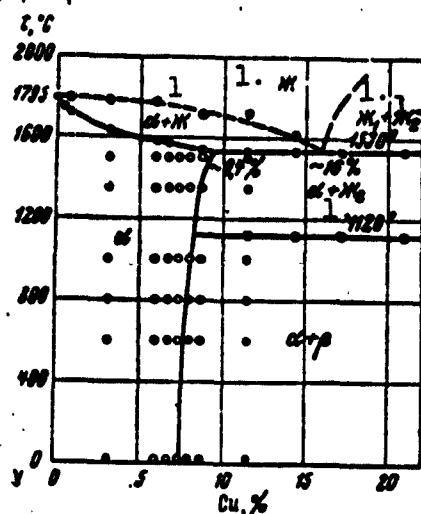for all V-Cu-C alloys containing 1.5% C by weight [8].



Fig. 5. Vertical section of
vanadium angle of phase dia-
gram of V-Cu-Al alloys having
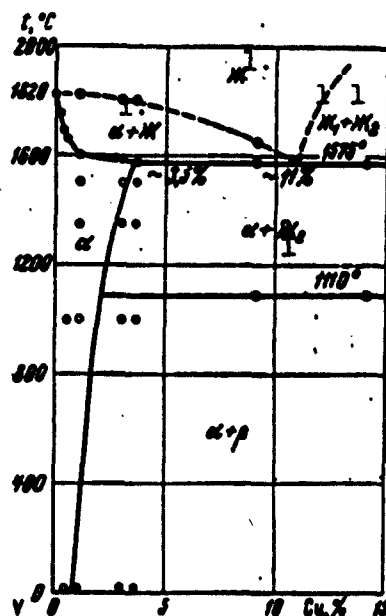constant aluminum content
(1.5% Al by weight). 1) zh.

Fig. 6. Vertical section of
vanadium angle of phase diagram
of V-Cu-C alloys having con-
stant carbon content (1.5% C
by weight). 1) zh.

Lines representing a solid solution of vanadium in copper were
seen on the X-ray diffraction patterns for V-Cu-C alloys containing
3.0 and 9.1% Cu by weight.

Vertical sections of the vanadium angle of the phase diagram
for a V-Cu-Al alloy (1.5% Al by weight) (Fig. 5) and a V-Cu-C alloy
(1.5% C by weight) (Fig. 6) have been constructed, using all avail-
able experimental data.

## CONCLUSIONS

Vertical sections of the vanadium angle of the phase diagrams
for V-Cu-Al and V-Cu-C systems with constant aluminum and carbon

contents (1.5% by weight) have been constructed from data obtained
by microstructural, thermal, and X-ray analyses and by investiga-
tions of certain mechanical properties of V-Cu-Al and V-Cu-C alloys.

Vanadium and copper form unsaturated solid solutions. At a
temperature of $20^{\circ}$, the limit of solubility of copper in alumino-
thermal vanadium is approximately 7.5% by weight. When the tempera-
ture is increased, the solubility of copper in the vanadium-based
solid solution increases, reaching a maximum (9.4% Cu by weight) at
a temperature of $1530^{\circ}$.

A broad region of stratification is observed in this system,
in the liquid and solid states, starting at the vanadium side when
the copper content is approximately 16% by weight. The monotectic
temperature is $1530^{\circ}$. The melting point of the solid solution of
vanadium in copper is $1120^{\circ}$.

The addition of 1.5% C by weight to the alloys causes a sharp
decrease in the solubility of the copper in the vanadium, this being
the result of the fact that there is no reaction between copper and
carbon. The limit of solubility of copper in carbon-containing
vanadium alloys is approximately 1% by weight at room temperature
and 3.5% by weight at $1575^{\circ}$. Copper increases the monotectic equilib-
rium temperature from 1530 to $1575^{\circ}$ and expands the region of im-
miscibility. The alloys are stratified, beginning at 11% Cu by weight.

Copper dissolved in vanadium increases the hardness of the
latter and, as was established for alloys containing carbon, reduces
its plasticity. The addition of copper to these alloys increases
their strength.

The addition of copper causes an increase in the lattice con-
stants of the vanadium solid solution. No new phases are detected
in the vanadium-copper-aluminum system besides those solid solutions

*101*

based on these metals. It has been established for alloys containing carbon that a second vanadium phase with a hexagonal lattice structure, apparently a γ-phase, is present in addition to the two solid solutions.

## REFERENCES

1. L. Gullet. Revue de Metallurgie [Metallurgical Review], 1906, 3, 174.

2. G.L. Norris. J. Franklin Inst., 1911, 171, 580.

3. H. Giebelhausen. Z. f. anorg. und allg. Chem. [Journal of Inorganic and General Chemistry], 1915, 91, p. 254.

4. A.G. Dowson. Abstract of Dissertation from University of Cambridge, 1936-1937, 115.

5. M. Hansen. Constitution of Binary Alloys. N.Y., 1958.

6. W. Rostoker, A. Yamamoto. Trans. ASM, 1954, 46, 1136.

7. W. Rostoker. The Metallurgy of Vanadium, N.Y.—London, 1958.

8. M.A. Gurevich, B.F. Ormont. Zh. Neorganich. khim. [Journal of Inorganic Chemistry], 1957, 2, Issue 7, pp. 1566-1580.

[List of Transliterated Symbols]

| Manuscript Page No. | | | | |
|---|---|---|---|---|
| 13 | cж | = szh = | szhatiye = | compression |
| 16 | ж | = zh = | zhidkost = | liquid |

# THE INFLUENCE OF TENSILE STRESSES ON THE CORROSION RATE OF METALS

By V.V. Romanov

The simultaneous action of tensile stresses and the electro-chemical corrosion of metals can increase or decrease the rate of corrosion or can change its nature, i.e., can cause extremely detrimental forms of local corrosion — corrosion fatigue and corrosion decrepitation. This explains the interest which investigators have manifested in the study of the stress factor in the corrosion of metals.

Despite the abundance of experimental data gathered together in the literature, at the present time one of the basic problems in this field has still not been sufficiently clarified. This is the question of the influence of static tensile stresses on the corrosion rate of metals.

In this article, an attempt is made to generalize the data on this problem, which occurs in the literature, and experimentally to study the influence of external tensile stresses on the corrosion rate of certain metals in neutral chloride solutions.

Apparently, the general opinion of researchers is that stress increases the corrosion rate of metals in acid media, regardless of whether the stress is internal or external, and that the increase in corrosion rate is an approximate linear function of the increase in stress [1-7].

According to the data of Skapskiy and Chizhevskiy [2], the in-

crease in corrosion rate in these media begins when the pH drops below 4.

However, there are exceptions to this general rule; Garre [1] observed that rolling reduced the corrosion rate of pure tin in hydrochloric acid. Evans [1] explained this by the fact that tin recrystallizes at comparatively lower temperatures after rolling and, consequently, the lattice structure of the rolled metal must be more perfect than that of the unrolled metal.

Ye.M. Zaretskiy [5] established that the corrosion rate of copper in a 0.1 mole solution of ammonium persulfate (pH = 2) decreased with an increase in the degree of tensile deformation.

According to the data of Fontana [8], stress does not increase the corrosion rate of stainless steel in fuming nitric acid at elevated temperatures.

Straumanis and Wang [9] established that specimens of pure (99.99%) cold-rolled aluminum had the same corrosion rate in 1 N hydrofluoric acid as did specimens of the same material subjected to preliminary recrystallization at temperatures of $40-575^\circ$.

The authors also established that the corrosion rate of aluminum is independent of the angle to the direction of rolling at which the specimens were cut.

The increase in corrosion rate in acid media under the action of stress is explained by the shift in the values of the electrode potentials of the metals to the negative side, by the redistribution of cathodic impurities, or by the mechanical breakdown of the protective films.

In addition, G.V. Akimov [10] suggested that the deformed metal yielded less work, i.e., the bond $Me^{+} \cdot \overline{e}$ was weakened and the ion $Me^{+}$ consequently left the lattice more easily than it could

in nondeformed metal.

For one particular case, an alloy of Al with 5% Mg or more, Mirs [11] attributed the increase in corrosion rate in the case of deformation to the liberation, from the Al-Mg solid solution, of a metallic compound which corroded quite rapidly in certain media.

The data in the literature on the influence of static stresses on corrosion rate in neutral salt solutions are somewhat contradictory, although the majority of authors have shown that stress has little or no effect on corrosion rate [4, 5, 9, 12-16].

Evans explained this by the fact that the majority of metals corrode in neutral salt solutions by oxygen depolarization and the rate of this process is determined by the diffusion of oxygen to the microcathodes.

Of course, the rate of oxygen diffusion is independent of the deformation of the metal.

The author found confirmation of this opinion in the fact that deformation had an effect on corrosion rate when oxygen was intensively supplied to the microcathodes as, for example, when the solution was agitated [1].

In a diffusion regime, the possible redistribution of cathode particles will have no effect on the corrosion rate, since N.D. Tomashov [17] has shown, when the degree of dispersion is small and the cathodes are uniformly distributed on the surface of the metal, virtually the entire possible electrolyte volume is used for the diffusion of oxygen to the corroding surface, even when the area of the microcathodes is rather small.

For the same reason, apparently, stress has no influence on the corrosion rate of a metal under atmospheric conditions [18, 19].

In accordance with these data, Mears, Brown, and Dix [20] and

Mirs [11] came to the conclusion that a static load less than the yield point has no influence on the corrosion rates of the majority of technical aluminum alloys under normal operating conditions.

Luz [21] expressed the same conclusion about magnesium and its alloys.

Evans [1] noted the fact that stress does not increase the corrosion rate of steel under atmospheric conditions and, on the contrary, often even reduces it.

This decrease is due to the large number of corrosion products and the fact that they adhere more closely to the surface of unstressed metal than to that of stressed metal and, as a result, the surface of unstressed metal dries no further and corrodes strongly.

The experimental data of Vedenkin and Gladyrevskaya [19] are in complete accordance with this conclusion. These data show that the corrosion rate of carbon steel decreases under atmospheric conditions when the tensile stress is increased from 0 to 16 $kg/mm^2$.

G.V. Akimov expressed the opinion that stress increases the corrosion rate of a metal: "A great deal of experimental material shows that stress and deformation always increase the corrosion rate" [22, page 175]. However, this opinion is confirmed only by the data of Krenig [4], other experiments in this direction not being considered. The data given show that this opinion is not exact.

The influence of stress on the electrochemical characteristics of metals is of great value for clarifying the mechanism by which stress influences the rate and nature of corrosion.

We know of attempts at a theoretical calculation of the possible change in reverse electrode potential of a metal during the course of certain work on deformation.

Carrying out such a calculation for a magnesium electrode under a stress of 17 kg/mm$^2$, Ye.M. Zaretskiy [23] obtained a value of 2.5 mv. Harwood [24], as well as D.V. Ryabchenkov and V.M. Nikiforova [25], obtained electrode potential changes of the same order as those calculated theoratically for the deformation of the metal.

Experimental verification has shown that both external and internal stresses change the electrode potential of the metal either very slightly or to tenths of a millivolt, i.e., up to values which cannot be associated with an increase in the internal energy supply of the metal [4, 21-31].

As a rule, the change in electrode potential under stress is observed in the first comparatively short time intervals, after which the potentials of stressed and unstressed metal converge [23, 31].

Researchers have noted that the electrode potential of a metal changes quite markedly under the action of stresses caused by plastic deformation and changes no more than 1-2 mv under the action of elastic stresses [31].

We know of experiments that were devised to investigate the influence of stress on the polarizability of magnesium [23], iron, and soft steel [29], and these have shown that stress and deformation do not materially change the polarizability of a metal.

The influence of stress on the electrochemical characteristics of a metal rests on the following circumstances. For example, G.V. Akimov has suggested that the film formed on stressed or deformed metal at the initial instant of electrolyte action contains more cracks of greater size than that formed on nondeformed metal, thus making it possible to debase the electrode potential of the metal [22].

## TABLE 1

The Chemical Composition and Certain Chemical Properties of the Metals Being Studied, %.

| Материал | Mn | Si | Fe | Zn | Cu | Mg | Al | C | S | Ni | P | Cr | Ti | $\sigma_e$, кг/мм² | удлинение, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Д-16, АМО | 0,03 | 0,41 | 0,87 | 0,5 | 4,55 | 1,66 | Ост | — | — | — | — | — | — | 23,1 | 18,3 |
| В-95А, ТНВ 1,5 | 0,34 | — | — | 5,5 | 1,50 | 2,15 | Ост | — | — | — | — | 0,19 | — | 25,3 | 17,5 |
| МА-8 | 2,32 | 0,19 | 0,17 | 0,03 | 2,236 | 0,т | 0,23 | — | — | 0,003 | — | — | — | 24,6 | 40,0 |
| МА-2 | 0,3 | 0,07 | 0,007 | 0,66 | 0,05 | 0,т | 3,4 | — | — | 0,0003 | — | — | — | 28,2 | 12,4 |
| Медь красная | — | — | — | — | — | — | — | — | — | — | — | — | — | 23,4 | 39,3 |
| Латунь | — | — | — | 38,3 | 62,5 | — | — | — | 0,098 | — | 0,01 | — | — | 33,7 | 65,2 |
| Железо техническое | 0,90 | 0,014 | Ост | — | — | — | — | 0,22 | 0,005 | — | 0,01 | — | — | 33,0 | 11,8 |
| Сталь 3 | 0,46 | 0,026 | 0,т | — | — | — | — | 0,1 | 0,042 | — | 0,02 | — | — | 42,0 | 32,4 |
| Сталь 1Х18Н9 | — | — | 0,т | — | — | — | — | 0,103 | — | 9,95 | — | 19,97 | 0,46 | 67,1 | 63,5 |

1) Material; 2) $\sigma_v$, kg/mm²; 3) elongation, %; 4) D-16, AMO; 5) V-95A, TNV 1.5; 6) cuprite; 7) brass; 8) technical iron; 9) steel 3; 10) steel 1Kh18N9.

An analogous idea was expressed by Evans and Simand [31]. In addition, Evans thinks that stress increases the internal energy supply of the metal.

In the experimental section of this work, the influence of stress on corrosion rate, electrode potential, and the kinetics of the electrode processes were studied.

Certain alloys, widely used in practice were selected as the subject for research (Table 1). These alloys were in the form of semifinished industrial products (sheets) and had not been subjected to special heat treatment.

The specimens were cut parallel to the direction of rolling and were of the conventional shape for tensile testing. Their surfaces were polished with successively finer grades of emory paper.

The final polishing was longitudinal and was carried out with grade 14 emory paper and the specimens were then degreased and treated in the following solutions:

Alloys based on magnesium, g/l:

$$1) \ CrO_3 \quad - \ 150,$$
$$2) \ NaNO_2 \quad - \ 20,$$

for 3 minutes;

alloys based on aluminum, %:

$$1) \ HNO_3 \quad - \quad 6,$$
$$2) \ K_2Cr_2O_7 \quad - \quad 1,$$

for 5 minutes;

alloys based on iron, %:

$$1) \ HF \quad - \quad 1,$$
$$2) \ HNO_3 \quad - \quad 5,$$

for 3 minutes;

copper and copper-based alloys:

1) $0.1$ N $HNO_3$

for 2 minutes, washed, dried, and agitated for 19-20 hours in a desiccator.

The working surface of the specimens was of two sizes: 100 x x 10 x 2 mm for laboratory tests for uniaxial tension and 50 x 10 x x 2 mm for the remaining specimens.

With tests under atmospheric conditions or in direct loading apparatus, the nonworking surfaces were insulated with BF-2 lacquer which was then dried at a temperature of $60^\circ$ for 3 hours, while for the other tests, in addition to BF-2 lacquer, a perchloral vinyl lacquer containing dibutyl phthalate as a filler was used.

For the laboratory tests, the specimens were vertically positioned and, by uniaxial elongation, their insulation was moved to 5 mm below the water level.

In the basic tests, stress was produced by uniaxial elongation of the specimens on lever machines [34] and on devices and machines adapted to set up uniaxial tension by the use of a weight or spring when the specimens are horizontally positioned [33, 35]. As a rule, the original stresses are selected so as to fall within the limits of elasticity.

For purposes of comparison, a number of the experiments were carried out with specimens bent into a curve with a constant depth of curvature, i.e., in the presence of nonuniform tensile stress distribution and residual deformation in the metal, phenomena foreseen as a consequence of the incomplete straightening of the specimens after bending.

The experiments were of a purely qualitative character and the maximum tensile stresses for a given case were not calculated.

In order to conduct these last experiments, the specimens were

fastened in curved textolite shoes by ebonite screws.

The surface adjoining the shoe was insulated, as was the non-working section of the specimens. The shoes and specimens were fastened to a variable loading wheel [32] or an ordinary variable loading unit.

In order to carry out uniaxial tension experiments on the specimens, the latter were placed in a beaker with a capacity of approximately 250 cm$^3$, being passed through a hole in the bottom of the beaker when vertically positioned and through holes in the side walls of the beaker when horizontally positioned. In both cases, hermetic sealing was effected with slitted rubber plugs.

The basic corrosive agent in the laboratory tests was 0.1 N NaCl prepared from chemically pure salts in distilled water, while main water was used as the corrosive agent in tests on the variable loading wheel.

For purposes of comparison, several experiments were carried out under atmospheric conditions in 0.1 N $H_2SO_4$ + 35 g/liter NaCl, 0.1 N NaCl + 10 g/liter $NH_4Cl$, and 5% HCl, which were also prepared from chemically pure salts in distilled water.

The corrosion rate was determined by the gravimetric method and by the amount of hydrogen evolved; in the latter case, a measuring burette was placed in the working flask beneath the horizontally positioned specimens. Weighing was carried out on damped analytical balances.

After the weight losses were determined, the corrosion products were removed from the specimens in the solutions described in reference [10].

Electrochemical characteristics were measured for the horizontally positioned specimens. The electrode potentials were meas-

111

sured by the compensation method. A saturated calomel electrode was used as the comparison electrode. The value of the electrode potential was converted to the hydrogen scale. An electrical system which made it possible to select the desired current flux was used. A platinum wire wound around the working portion of the specimens was used as the auxiliary electrode. The laboratory tests were conducted at room temperature.

Fig. 1. The influence of tensile stresses on the corrosion rate of D-16 alloy in a 0.1 N solution of NaCl for 1000 hours. 1) Corrosion rate after 1000 hours, $mg/cm^2$; 2) stress, $kg/mm^2$.

Fig. 2. The effect of tensile stresses on the corrosion rate of D-16 alloy in a solution of 0.1 N $H_2SO_4$ + 35 g/l NaCl, after 180 min. 1) Corrosion rate after 180 min., $cm^3/cm^2$; 2) stress, $kg/mm^2$.

In order to consider the influence of stress on corrosion rate, the mean data from five parallel measurements were used, while that from three parallel measurements were used for the consideration of electrochemical characteristics.

Investigation of the influence of stress on the corrosion rate of metals was carried out by two methods: 1) by studying the influence of stresses of various magnitudes on the corrosion rate of metals when all other conditions remain identical; 2) by comparing the corrosion rates of specimens in the stressed and unstressed states, after an arbitrarily selected time interval. The second method includes the setting up of stresses either by uniaxial ten-

sion or by bending.

Data on the influence of stress on the corrosion rate of D-16 alloys in 0.1 N NaCl for 1000 hours (Fig. 1) shows that stresses up to 13 kg/mm$^2$ have virtually no effect on corrosion rate and cause a certain slight increase in corrosion rate only when they approximate the yield point, and this is most readily explained by the intensification of purely mechanical fracture in the protective film and the increase in size of the corroding surface by the elongation of the specimens, which results from the appearance of plastic deformation.

For purposes of comparison, Fig. 2 shows data on the influence of stress on the corrosion rate of the same alloy in an NaCl solution acidified with 0.1 N sulfuric acid. As may be seen, in this case, the stress directly increases the corrosion rate of the metal. For a period of 180 minutes, this function is linear in character.

TABLE 2

Influence of Uniaxial Stress on Corrosion Rate of Metals (vertical positioning of specimens)

| 1 Металл | 2 Среда | 3 Напряжение, кг/мм² | 4 Продолжительность испытания, час | 5 Потери веса, мг/см² |
|---|---|---|---|---|
| MA-2 | 0,1 н NaCl | 10 | 540 | 5,9 |
| MA-2 | То же | 0 | 540 | 5,4 |
| Ст. 3 | » » | 15 | 110 | 8,2 |
| Ст. 3 | » » | 0 | 1104 | 14,0 |
| Д-16 | » » | 13 | 1000 | 0,4 |
| Д-16 | » » | 0 | 1000 | 0,39 |
| Ст. 1X18Н9 | » » | 25 | 1000 | — |
| Ст. 1X18Н9 | » » | 0 | 1000 | — |
| В-95 | » » | 15 | 1000 | — |
| В-95 | » » | 0 | 1000 | — |
| Медь красная | 5 % HCl | 10 | 113 | 26,8 |
| То же | То же | 0 | 113 | 24,4 |
| Латунь | 0,1 н NaCl + 10 г/л NH₄Cl | 15 | 1152 | 180,0 |
| То же | То же | 0 | 1152 | 176,0 |

1) Metal; 2) medium; 3) stress, kg/mm$^2$; 4) duration of test, hours; 5) weight loss, mg/cm$^2$; 6) 0.1 N NaCl; 7) the same; 8) steel 3; 9) D-16; 10) steel 1Kh18N9; 11) V-95; 12) cuprite; 13) brass; 14) 0.1 N NaCl + 10 g/l NH₄Cl.

The data shown in Table 2 also attest to the small influence of elastic stresses on the corrosion rate of metals with the exception of steel 3 in a 0.1 N NaCl solution. The results obtained for steel 3 have been verified in repeated tests but it is difficult to explain an exception of this type by the general rules.

The data of the influence of stress on the corrosion rate of copper in a 5% HCl solution given in Table 2 for purposes of comparison more clearly show the aforementioned increase in corrosion rate under the action of stresses.

The same results were obtained for brass when testing in a solution of 0.1 N NaCl + 10 g/liter $NH_4Cl$.

The increase in corrosion rate under the influence of tensile stresses in a 0.1 N NaCl solution manifests itself somewhat more clearly when the stresses are created by bending (Table 3) and this undoubtedly is a result of the presence of a nonuniform distribution of stresses and plastic deformation in the metal, i.e., conditions which facilitate failure of the protective film on the surface of the metal as compared with uniaxial elastic tension applied to the specimens.

The data in Table 4 attest to the slight influence of elastic tensile stresses on the corrosion rate of metals under atmospheric conditions and this is in complete accordance with the data adduced by other investigators. The data on steel 1Kh18N9 is an exception. In contrast to the smooth surface of unstressed specimens of this steel, the surface of stressed specimens is covered with a large number of deep pits. Apparently, this indicates that the role of stress in the corrosion of metals consists in its action on the protective film, in this case, in weakening it. Measurement of the electrode potentials of the metals in time made it possible to

establish that stress has the greatest influence on the electrode

during the first few minutes of measurement. The influence of

stress proves to be substantially less in the region of stationary

electrode potential values.


TABLE 3

Influence of Plastic Deformation and Nonuniform Stressed Distribu-
tion on the Corrosion Rate of Metals*

| Металл [1] | Среда [2] | Стрела прогиба [3] | Продолжительность испытания, час. [4] | Потеря веса, мг/см³ [5] | Прибор, на котором производились испытания [6] |
|---|---|---|---|---|---|
| Ст. 3 [7] | 3 % NaCl [13] | 8 | 1056 | 39,6 | Колесо переменного [17] |
| Ст. 3 [7] | То же | 0 | 1056 | 37,2 | погружения |
| Д-16 [8] | » » | 8 | 2886 | 5,6 | То же |
| Д-16 [8] | » » | 0 | 2886 | 12,4 | » » |
| Ст. 1Х18Н9 [9] | » » | 8 | 2886 | — | » » |
| Ст. 1Х18Н9 [9] | » » | 0 | 2886 | — | » » |
| В-95 [10] | » » | 8 | 272 | 0,39 | » » |
| В-95 [10] | » » | 0 | 272 | 0,37 | » » |
| Железо техническое [11] | » » [15] | 8 | 960 | 39,0 | » » |
| | » » | 0 | 960 | 37,0 [18] | » » |
| Медь красная [12] | 35 г/л + 35 г/л NH₄Cl [13] | 8 | 156 | 117,0 | Аппарат переменного погружения |
| То же [13] | То же [13] | 0 | 156 | 74,2 | То же [13] |
| Латунь [14] | 0,1н. NaCl + 10 г/л NH₄Cl [16] | 8 | 787 | 16,2 | » » |
| То же [13] | То же [13] | 0 | 787 | 15,7 | » » |

*Specimens bent into a curve.

1)Metal; 2) medium; 3) depth of curvature; 4) duration of test,
hours; 5) weight loss, mg/cm²; 6) instrument on which tests were
carried out; 7) steel 3; 8) D-16; 9) steel 1Kh18N9; 10) V-95;
11) technical iron; 12) cuprite; 13) the same; 14) brass;
15) 35 g/l + 35 g/l NH₄Cl; 16) 0.1 N NaCl + 10 g/l NH₄Cl;
17) variable-load wheel; 18) variable-load equipment.

The data for the D-16 alloy given in Fig. 3 show that the

action of stress materially alters the shape of the potential –

time curve. It is obvious that as the stress increases the char-

acteristic section of the curve which describes the original de-

basement of the electrode potential value is shortened and, at a

stress of 15 $kg/mm^2$, disappears completely.

Stress also has a substantial effect on the electrode poten-

tial of MA-2, although this is smaller for the other alloys studied.

Apparently, the data obtained for D16 alloys also indicates

that the action of stress changes the conditions for the formation

of stable protective films on the surfaces of the metals.

TABLE 4

Influence of Uniaxial Stress on the Corrosion Rate of Metals Under
Atmospheric Conditions*

| Металл | Исходные напряже-ния, кг/мм² | Продолжи-тельность ис-пытаний, час. | Потеря веса, мг/см² | Металл | Исходные напряже-ния, кг/мм² | Продолжи-тельность ис-пытаний, час. | Потеря веса, мг/см² |
|---|---|---|---|---|---|---|---|
| Латунь | 18 | 2232 | 91,0 | Ст. 3 | 0 | 2160 | 11,7 |
| То же | 0 | 2232 | 91,0 | Д-16 | 10 | 2160 | 13,5 |
| MA-8 | 10 | 1160 | 2,8 | Д-16 | 0 | 2160 | 12,4 |
| MA-8 | 0 | 1160 | 3,1 | Ст. 1Х18Н9 | 20 | 2208 | 0,46 |
| Ст. 3 | 15 | 2160 | 13,5 | Ст 1Х18Н9 | 0 | 2208 | 0,072 |

*Corrosion-testing area on the grounds of the A.A. Baykov Metal-
lurgy Institute of the Academy of Sciences USSR.

1) Metal; 2) initial stress, $kg/mm^2$; 3) duration of tests, hours;
4) weight loss, $mg/cm^2$; 5) brass; 6) the same; 7) steel 3; 8) D-16;
9) steel 1Kh18N9.

Fig. 3. Influence of tensile
stress on the electrode poten-
tial of D-16 alloy in 0.1 N
solution of NaCl; 1) $\sigma = 0$
$kg/mm^2$; 2) $\sigma = 10$ $kg/mm^2$;
3) $\sigma = 15$ $kg/mm^2$; 4) elec-
trode potential, mv;
5) time, minutes.

Fig. 4. Influence of tensile
stress (for 180 minutes) on
electrode potential of a series
of metals in 0.1 N NaCl. 1) Elec-
trode potential, mv; 2) stress,
$kg/mm^2$; 3) brass.

Data on the influence of stress on the electrode potentials

of metals in the stationary-value regions (for 180 minutes) show

(Fig. 4) that this influence is small and can be explained by the

intensification of the failure of the protective films on the sur-
faces of the metals.

Fig. 5. Influence of tensile
stress on polarization of
D-16 alloy in 0.1 N NaCl.
1) $\sigma = 10$ kg/mm$^2$; 2) $\sigma =$
$= 0$ kg/mm$^2$; 3) electrode
potential, mv; 4) polari-
zation $D_{k.a}$, ma/cm$^2$.

Fig. 6. Influence of tensile
stress on polarization of
technical iron in 0.1 N NaCl.
1) $\sigma = 0$ kg/mm$^2$; 2) $\sigma = 10$ kg/mm$^2$;
3) $\sigma = 20$ kg/mm$^2$; 4) electrode
potential, mv; 5) polarization
$D_{k.a}$, ma/cm$^2$.

The specimens began to polarize after they had been exposed
to the solution for 180 minutes.

Stress has little effect on the polarizability of D-16 alloys
and iron (Figs. 5 and 6). Data on brass (Fig. 7) indicate that
stress somewhat reduces both the cathodic and anodic polarizability
of the alloy.

CONCLUSIONS

1. In nonoxidizing acid media, stress increases the corrosion
rate of metals linearly. However, there are the exceptions to this
rule which we have considered, where stress does not increase the
corrosion rate, but on the contrary decreases or has no effect on
it.

2. Elastic stresses have virtually no effect on the corrosion

rate of metals in 0.1 N NaCl and under atmospheric conditions.

The presence of plastic deformations and the nonuniform stress distribution facilitates a certain increase in the corrosion rate of metals under these conditions.

3. Stress has little effect on the electrode potentials of metal and on the kinetics of the electrode processes in 0.1 N NaCl.

Fig. 7. Influence of tensile stress on polarization of brass in 0.1 N NaCl. 1) $\sigma = 10$ kg/mm$^2$; 2) $\sigma = 0$ kg/mm$^2$; 3) electrode potential, mv; 4) polarization $D_{k.a}$, ma/cm$^2$.

4. The action of elastic tensile stresses in the corrosion of stressed metals consists chiefly in changing the conditions for the formation of a protective film on the surface of the metal.

### REFERENCES

1. U.R. Evans, Metallic Corrosion, Passivity and Protection, 1946, p. 483.

2. M.T. Simand, U.R. Evans. Trans. Faraday Soc., 1950, 46, 3, 175.

3. G. Tamman, F. Neubert, Ztschr. Anorg. Chem. [Journal of Inorganic Chemistry], 1932, 207, 87, 8, 8.

4. V.O. Krenig, Korroziya metallov [Corrosion of Metals], izd. ONTI-NKTP [United Scientific and Technical Publishing Houses - Peoples Commisariat of Heavy Industry], 1936, p. 88.

5. Ye.M. Zaretskiy, Zh. neorganich. khim. [Journal of Inorganic Chemistry], 1951, 24, No. 5.

6. V.P. Severdenko, Metallurg, [The Metallurgist], 1947, No. 7 (91), p. 53.

7. G. Ulig, Korriziya metallov [Corrosion of Metals], Collection 1, Leningrad-Msocow, 1952, p. 30.

8. M.C. Fontana, Corrosion, Technology, 1957, 4, No. 12, 423.

9. M.E. Straumanis, Y.N. Wang, Corrosion, 1956, 12, No. 4, 39.

10. G.V. Akimov, Teoriya i metody issledovaniya korrozii metallov [Theory of and Research Methodology for the Corrosion of Metals], izd-vo AN SSSR [Academy of Sciences USSR Press], 1945, p. 175.

11. R. Mirs, Korroziya Metallov, Collection 1, Leningrad-Moscow, 1952, p. 123.

12. N.D. Tomashov, V.A. Titov, Korroziya metallov i metody bor'by s nei [Corrosion of Metals and Methods of Control], Oborongiz [State Publishing House for the Defense Industry], 1956, p. 26.

13. M.A Hunter, Metals Handbook, ASM, 1948, 134.

14. G. Edeleann. J. Inst. Met., 1951, 80, 187.

15. M.A. Scheil, Symposium on Stress Corrosion Cracking of Metals, 1944, 395 (ASTM, AJME).

16. G.L. Shvarts, Collection Prepared by the NIIKhIMMASh [Scientific Research Institute for Chemical Machinery], 1954, No. 17, p. 133.

17. N.D. Tomashov, Korroziya i zashchita metallov [Corrosion and Protection of Metals], Ch. 1, 1952, p. 117.

18. G.J. Metcalf, J. Inst. Metals, 1953, 1, 269.

19. S.G. Vedenkin, Gladyrevskaya, Bor'ba c korroziyey metallov na zheleznodorozhnom transporte [Prevention of Metal Corrosion in Railroad Transportation], Collection 57, Transzheldorizdat [State Publishing House for Railroad Transportation Literature], 1952.

20. R.B. Mears, R.H. Brown, E.H. Dix, Symposium of Stress-Corro-

sion Cracking of Metals, 1944, 323.

21. U. Luz, Korroziya metallov, Collection 1, 1952, p. 135.

22. G.V. Akimov, Teoriya i metody issledovaniya korrozii metal-lov, izd-vo AN SSSR, 1945, p. 175.

23. Ye.M. Zaretskiy, Zh. prikl. khim. [Journal of Applied Chemistry], 1951, 24, No. 6, p. 614.

· 24. J.J. Harwood, Corrosion, 1950, 5-6, No. 8.

25. D.V. Ryabchenkov, V.M. Nikiforova, Metallovedeniye i obra-botka metallov, 1956, No. 8, p. 2.

26. Wiedeman, Lehre von Electrizitaet [Theory of Electricity], 1893, 9, 727.

27. L.V. Nikitiv, Zh. obshch. khim. [Journal of General Chemis-try], 1936, 9, p. 975.

28. G.V. Akimov, Z.A. Vrutsevich, Tr. VIAM [Transactions of the All-Union Scientific Research Institute for Aviation Materials], 1936, 39, 37.

29. M.T. Simand, U.R. Evans, Trans. Faraday Soc. 1950, 46, p. 3, 175.

30. R.B. Mears, Metal Progress, 1945, 48, 105.

31. M.T. Simand, U.R. Evans, Proc. Roy. Soc., 1947, 188A, 372.

32. V. V. Romanov, K.N. Mel'nikov, ITEI AN SSSR, seriya 21 [Institute of Technical and Economic Information, Academy of Scien-ces USSR, Series 21], No. T-56-381/11.

33. V. V. Romanov, V.Ye. Bukhareva, ITEI AN SSSR, Vol. 9, No. II-56-491.

34. V.V. Romanov, ITEI AN SSSR, Theme 13, No. M-58-257/26.

35. V.V. Romanov, ITEI AN SSSR, Theme 13, No. M-59-362/33.

# THE INFLUENCE OF POLARIZATION AND PB-5 INHIBITOR ON THE
## CORROSIVE DECREPITATION OF CARBON STEELS

By S.B. Fel'gina and V.V. Romanov

In this work, as in preceding works [1, 10], we have set our-
selves the task of studying the influence of polarization and the
organic  inhibitor PB-5 on the rate of corrosive decrepitation of
a metal and the effect of polarization on the nature of corrosion
cracks.

Data are given in the literature on several investigations
[2-7] devoted chiefly to the qualitative study of the protective
action of cathodic polarization in the corrosive decrepitation of
carbon steels.

Makdonal'd and Veber [2] cited data which show that it is
possible materially to retard the corrosive decrepitation of low-
carbon steels in nitrate solutions by cathodic and protector in-
hibition. Kristal' [3] reports that it is possible to prevent the
decrepitation of carbon steels in boiling sodium nitrate solutions
by protector inhibition.

Parkins [4] reports that it is possible to avoid the corrosive
decrepitation of soft steels in boiling ammonium and calcium nitrate
solutions by cathodic polarization.

In experiments which well reproduced actual conditions, Weir
[5] observed that boiler plate subjected to uniaxial tension and
the action of 41.6 and 50% solutions of NaOH at temperatures of

250 and 280° were protected from decrepitation by cathodic polarization of the external current source. On the other hand, anodic polarization accelerates failure.

S.G. Vedenkin and L.S. Lebedeva [6] discovered that it was possible to protect soft steels from corrosive decrepitation by cathodic polarization under steam-boiler operating conditions, while Champion [7] discovered that this held true in the extraction of aluminum from ores with alkaline solutions.

The data cited have made it possible to establish the ability to retard the corrosive decrepitation of carbon steels by cathodic polarization and to accelerate it by anodic polarization.

The qualitative study of this relationship has aroused definite interest.

As the subject for our research, we selected type St. 3 carbon steel (see below) in semifinished sheets (sheet thickness, 2 mm).

Chemical Composition of Steel Being Studied, %

| C | Mn | Si | S | P | Fe |
|------|-------|------|-------|-------|-----------|
| 0.170 | 0.320 | 0.02 | 0.026 | 0.005 | remainder |

The method of research was quite similar to that used earlier in investigating the influence of polarization [8] and of the organic inhibitor PB-5 [10] on the corrosive decrepitation of type 18-8 stainless steel.

However, there was one difference; directly after testing, the carbon steel specimens were pickled in a solution of 5% $HNO_3$ + 1% HF and were then placed in a desiccator for 18-20 hours. A solution of 600 g/liter Ca $(NO_3)_2$ + 600 g/liter $NH_4NO_3$ + 50 g/liter $MnCl_2$ was selected as the corrosive agent.

The experiments were carried out at the boiling point (128°); the volume of solution was 200 $cm^3$, the working surface was 7.2 $cm^2$,

and the initial stress was 33 $kg/mm^2$; the pH of the solutions was measured by a glass electrode and an LP-5 potentiometer.

The electrode potentials were measured by the compensation method. The potential was measured in relation to a saturated calomel half-cell. 250 mv were subtracted from the obtained potential values.

The polarization curves were taken at room temperature and at the boiling point of the solution. The temperature jump of potential at the hot solution-cold solution boundary was not calculated, since interest centered on the relative change in the polarizability of the metal.

Data on the influence of cathodic polarization on the rate of corrosive decrepitation of steel (Fig. 1) show that the functional expression of these two factors has a characteristic shape: a first section is observed at current fluxes of 0.005 $ma/cm^2$, a second is observed in the interval 0.15-1.00 $ma/cm^2$, and a third* is found at 1.5 $ma/cm^2$ (the arrow on the diagram denotes that the specimens had not failed at the time indicated).

In order to satisfy ourselves that the protective action of cathodic polarization was not a result of possible changes in the medium or the protective films, the protective current was passed for less than three hours in individual experiments. After the current was shut off, the specimens soon failed.

Data on the influence of anodic polarization on the rate of corrosive decrepitation of steel (Fig. 1) show that decrepitation is observed only at small current fluxes, widely scattered data being obtained in this case. In essence, with current fluxes DA $\geq$ 0.1 $ma/cm^2$, decrepitation ceases. At the same time, a thick film of corrosion products, black in color, appears on the surface

of the metal and increases in thickness as the current flux is
increased. The fact that the polarization curve was taken in the

Fig. 1. The effect of cathodic
and anodic polarization on the
rate of corrosive decrepita-
tion of St. 3 steel in a boil-
ing solution of 600 g/liter
$Ca (NO_3)_2$ + 600 g/liter
$NH_4NO_3$ + 50 g/liter $MnCl_2$.
1) Time, minutes.

Fig. 2. Anodic polarization
curves for St. 3 steel in a
solution of 600 g/liter Ca
$(NO_3)_2$ + 600 g/liter $NH_4NO_3$ +
50 g/liter $MnCl_2$. 1) At room
temperature; 2) at boiling point
of solution (128°); 3) elec-
trode potential, $E_p$, v.

solution being studied (Fig. 2) showed that the anodic polarizability
of the metal in the hot solution was substantially greater than its
polarizability at room temperature.

The original acidic pH value of the solution (1.46) shifted
toward even more acidic values as the anode-current flux was in-
creased and, at 20 $ma/cm^2$, rapidly became less than 0 [sic].

Research has shown that cracks have an intergranular character
both with polarization and without.

In the absence of polarization, intergranular cracks (Fig. 3a)
are branched and curved; with anodic polarization (Fig. 3b), they

Fig. 3. Corrosion cracks in steel 3 (X 200).
a) Without polarization; b) with anodic polari-
zation; c) with cathodic polarization, insuf-
ficient for protection.

acquire a high degree of rectilinearity and continuity and become
comparatively narrower, especially at their origins; with cathodic
polarization (Fig. 3c) the cracks are wider and more branched than
when there is no polarization and have a tendency to expand laterally
along the grain boundaries and body, a phenomenon quite marked even
near the origins of the cracks.

When 0.1% PB-5 inhibitor was introduced into the solution
being studied, decrepitation did not set in after 540 minutes.

The influence of cathodic polarization on the rate of corrosive decrepitation in the steel being studied was analogous in character to that which was earlier established for other metals [1], a fact which can be demonstrated.

A quantitative comparison of data obtained for carbon steels in a boiling solution of calcium and ammonium nitrates to which manganese chloride was added with analogous data [1] for type 18-8 stainless chromium-nickel steel subjected to corrosive decrepitation in a boiling solution of $MgCl_2$ has made it possible to establish that all characteristic sections of the cathodic polarization curves for carbon steels are at higher current fluxes; thus, for example, the third section (Fig. 1), which characterizes the protective current flux for stainless steel, is at DK $\geq$ 0.13 ma/cm$^2$, while that for carbon steel is at DK $\geq$ 1.

There is only one possible explanation for this — the more intensive action of corrosive vapors on carbon steel than on stainless steel.

This can in turn be explained by the higher corrosion stability of nickel austenite as compared with the ferrite-perlite structure of the carbon steel under consideration, as well as by the greater aggressiveness (in particular, the substantially more acid pH value) of the electrolyte in which the corrosive decrepitation of the metal was studied.

The influence of anodic polarization is not characteristic, i.e., it is unusual in comparison with data for other metals. Anodic polarization does not accelerate corrosive decrepitation but, on the contrary, stops it.

Apparently, there is no doubt of the fact that the influence of anodic polarization is a result of the formation of a thick film

of black corrosion products on the surface of the metal. The formation of these products depends to a greater extent on the composition of the solution and the course of the electrolytic anodic reaction in the metal than it does on the individual properties of the metal itself; this is attested to by the fact that during the process of the cathodic polarization of the steel the same film is formed on the platinum wire which is used as an auxiliary electrode in polarization. Experiments have shown that the formation of this film causes a strong anodic polarization of the metal and this reduces the efficiency of the corrosive vapors (formed by the anode sections at the bottom of the original points of stress concentration and the corrosion cracks having cathode sections), affecting the rate of corrosive decrepitation of the metal [9].

Apparently, the process of forming a black film on the surface of carbon steel is facilitated by a low pH value of the solution and its further reduction during polarization, as well as by high solution temperature, and this is confirmed by the low polarizability of the metal at room temperature.

Data obtained on the influence of polarization on the character (shape) of corrosion cracks is of special interest, since it shows the influence of polarization on the intergranular character of decrepitation in contrast to those data which were obtained for the intergranular or composite character of the cracks [1, 8].

Despite the basic difference in the intergranular mode of corrosion crack development, the nature of the effect of polarization is in essence the same as that for intragranular decrepitation; this influence is manifested first of all at the bottom (origin) of the crack and, in cathodic polarization, leads to a tendency of

the crack to expand laterally along the body and the grain boundaries, while in anodic polarization, the cracks become elongated, compacted, and more rectilinear than those which developed in the nonpolarized metal in the absence of polarization.

The data obtained on the protective influence of PB-5 inhibitor in the corrosive decrepitation of carbon steel in nitrate solutions is very remarkable, since it was established earlier [10] that this inhibitor, at the same concentration (0.1%), protected type 18-8 stainless chromium-nickel steel in a boiling 42% solution of $MgCl_2$ from decrepitation. This gives us reason to assume that this use of PB-5 inhibitor is a general-purpose method for protecting iron-based alloys from corrosive decrepitation.

It is to be expected that the effect of the use of PB-5 inhibitor will be intensified as temperature is reduced. Its use at higher temperatures without further testing is inadvisable.

## CONCLUSIONS

1. It has been established that type St. 3 steel can be protected from corrosive decrepitation in a boiling solution of 600 g/liter $Ca(NO_3)_2$ + 600 g/liter $NH_4NO_3$ + 50 g/liter $MnCl_2$ by cathodic polarization (DK $\geq$ 1.5 ma/cm$^2$).

The expression of the rate of metal decrepitation as a function of current density (flux) has a characteristic shape.

2. Anodic polarization at current fluxes greater than 0.1 ma/cm$^2$ stops decrepitation. This is a result of the formation of a dense film of black corrosion products on the surface of the metal.

3. The influence of polarization on the character of intergranular corrosion cracks has been established. This effect is basically the same as that for intragranular or composite decrepitation of other metals.

## REFERENCES

1. V. V. Romanov, Sb. tr. Voronezhskogo khim. o-va [Collection Voronezh Chemical Society], Issue II, 1959.

2. Kh.D. Makdonal'd, D.T. Veber, Korroziya metallov [Corrosion of Metals], Goskhimizdat [State Scientific and Technical Publishing House for Chemical Literature], 1952, p. 436.

3. M.M. Kristal', Sb. NIIKhIMMASh [Collected Papers of the State Scientific Research Institute for Chemical Machinery], No. 25, p. 102.

4. R.N. Parkins, J. Iron and Steel Inst., 172, 149-162.

5. C.D. Weir, Applied Mechanics, 163, No. 55, 18.

6. S.G. Vedenkin, D.S. Lebedeva, Bor'ba c korrosiyey metallov na zheleznodorozhnom transporte [Prevention of Metal Corrosion in Railroad Transportation], Issue 57, Moscow, Transzheldorizdat [State Publishing House for Railroad Transportation Literature], 1952, p. 83.

7. F.A. Champion, Chem. a. Industry, 1957, No. 28, p. 967-975.

8. V.V. Romancv, V.V. Dobrolyubov, Metallovedeniye i obrabotka metallov [Metallography and Metals Processing], 1958, No. 7, p. 19.

9. V.V. Romanov, Sb. "Korrozionnoye rastreskivaniye metallov" [Collection The Corrosive Decrepitation of Metals], Mashgiz [State Scientific and Technical Publishing House for Literature on Machinery], Noscow, 1960, p. 24.

10. S.A. Balezin, V.V. Romanov, H.I. Podobayev, Dokl. AN SSSR [Proceedings of the Academy of Sciences USSR], 1958, 123, No. 5, p. 902.

[Footnotes]

Manu-
script
Page
No.

105   *The protective current flux was conditionally calculated

as that flux at which no decrepitation set in for a

period three times as long as that required for corro-

sion to begin in the absence of polarization.

# THE STRUCTURE AND PROPERTIES OF ALLOYS AT THE NIOBIUM
## CORNER OF THE NIOBIUM-VANADIUM-ALUMINUM SYSTEM

By V.V. Baron, M.I. Agafonova, and Ye.M. Savitskiy

Niobium is a material used in atomic power installations and jet propulsion engineering. One of the principle drawbacks of niobium is its low resistance to atmospheric oxidation at elevated temperatures. Consequently, research on the influence of alloying on the heat resistance, structure, and properties of niobium is of pressing importance.

We know from the data in the literature that the alloys in the niobium-vanadium system form a continuous series of solid solutions [1-3]. In addition, vanadium considerably increases the resistance of niobium to atmospheric oxidation [4, 5] at elevated temperatures (alloys containing 7.5 atom % vanadium at a temperature of $1000^{\circ}$ and 12.5 atom % vanadium at $1200^{\circ}$). We established some time ago that niobium forms three compounds with aluminum: $Nb_3Al$, $Nb_2Al$, and $NbAl_3$ [6].

The solubility of aluminum in solid niobium is 5% at room temperature. In the solid solution region, aluminum increases the corrosion resistance of niobium to water vapor at a temperature of $600^{\circ}$. There are reports [7] that aluminum has a positive effect on the heat resistance of niobium at temperatures of 1000 and $1200^{\circ}$.

There are no data in the literature on the structure and properties of the alloys in the ternary niobium-vanadium-aluminum system.

This work deals with the structure and properties of the alloys at the niobium corner of the niobium-vanadium-aluminum system which contains up to 10% V and Al by weight.

Metalloceramic niobium was used as the original material (Table 1).

TABLE 1
Chemical Composition of Niobium, % by Weight.

| Элемент | % | Элемент | % |
|---|---|---|---|
| Ниобий .... | 99,1 | Азот .... | 0,1 |
| Тантал. .... | 0,4 | Углерод .. | 0,08 |
| Титан ..... | 0,14 | Кислород . | 0,07 |
| Железо. .... | 0,085 | Свинец ... | 5,10⁻⁸ |
| Кремний. ... | 0,04 | | |

1) Elements; 2) niobium; 3) tantalum;
4) titanium; 5) iron; 6) silicon;
7) nitrogen; 8) carbon; 8) oxygen;
9) lead.

The aluminothermal vanadium used contained 96.5% V, 1.5% Al, 0.15% Fe, 0.05% Cu, 0.3% Si, 0.1% Mn, 0.27% N, and a significant quantity of oxygen. The aluminum used was 99.99% pure.

The alloys were prepared in an arc furnace on a copper water-cooled bottom (sole), by a nonconsumable tungsten electrode in a purified helium atmosphere.

Each ingot weighed 50 g. An excess of aluminum, up to 30% greater than the amount calculated to be necessary, is added to the charge to compensate for the possible loss of aluminum in melting, since the vaporization point of aluminum ($2000^\circ$) is lower than that of niobium ($2400^\circ$). The ingots were turned over and remelted several times in order to obtain alloys of uniform composition. The use of arc melting made it possible to prepare alloys over the entire concentration range. We prepared 35 alloys (Table 2).

TABLE 2

Composition of Alloys, % by Weight

| Сплав | Состав сплава | | Сплав | Состав сплава | |
|---|---|---|---|---|---|
| | V | Al | | V | Al |
| 1 | 0 | 0 | 18 | 5,2 | 1,0 |
| 2 | 1 | 0 | 19 | 3,5 | 1,85 |
| 3 | 0,67 | 0,33 | 20 | 1,8 | 3,28 |
| 4 | 0,5 | 0,5 | 21 | 9,0 | 0 |
| 5 | 0,3 | 0,49 | 22 | 6,8 | 1,19 |
| 6 | 0 | 0,57 | 24 | 2,2 | 4,76 |
| 7 | 3 | 0 | 25 | 3,44 | 6,82 |
| 8 | 2,2 | 0,6 | 26 | 0,4 | 3,29 |
| 9 | 1,5 | 0,87 | 27 | 0,5 | 6,74 |
| 10 | 0,8 | 0,86 | 28 | 2,2 | 3,36 |
| 11 | 0 | 2,2 | 29 | 0,7 | 9,55 |
| 12 | 5,0 | 0 | 30 | 1,2 | 14,13 |
| 13 | 3,7 | 0,5 | 31 | 4 | 5,15 |
| 14 | 2,5 | 0,91 | 32 | 3 | 9,01 |
| 15 | 1,3 | 1,92 | 33 | 6 | 3 |
| 16 | 0 | 4,05 | 34 | 6,71 | 2,66 |
| 17 | 7,0 | 0 | 35 | 1 | 5,23 |

1) Alloys; 2) composition of alloy.

The alloys were studied in the cast, annealed, and quenched states. Annealing was carried out in evacuated double quartz ampules for 50 hours in a Silit furnace at a temperature of 1100° with subsequent cooling as the furnace cooled. The alloys were quenched in a TVV [not identified in standard references] vacuum furnace at a temperature of 1600° and soaked for 3 hours.

The cross sections for microstructural analysis were prepared by the usual method. All the alloys were pickled in a mixture of concentrated HF and HCl.

Hardness was measured on a Vickers apparatus, with a load of 10 kg.

The microhardness of the alloys was measured on a PMT-2 apparatus, with a load of 50 g.

X-ray diffraction investigations were carried out on the annealed alloys in a Debye chamber, using nickel radiation.

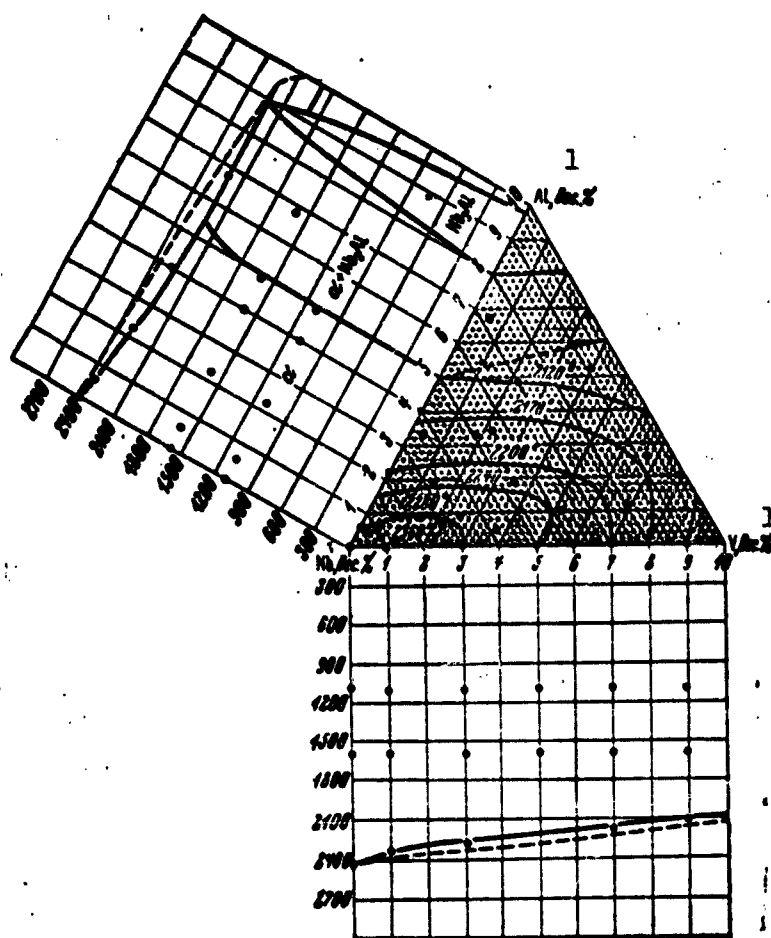The melting points of the alloys were determined by the drop

Fig. 1. Isothermal section at 20° of niobium corner
of phase diagram of niobium-vanadium-aluminum system
and projection of solidus isotherms on concentration
triangle of system. 1) % by weight.

method, using an optical pyrometer; the temperature at which the
first molten drop appeared in an aperture drilled in the center of
the specimen was measured, the depth to diameter ratio of this aper-
ture being approximately 4, thus ensuring conditions approximating
those which obtain for an ideal (absolute) black body.

The heat resistance of the alloys was investigated at tempera-
tures of 1000 and 1200° with soaking for 1-4 hours. The specimens
for these tests were rectangular in shape and 10 x 5 x 5 mm in size.
Before testing, the specimens were polished with #14 emery paper.
The heat resistance tests were carried out in corundized crucibles

134

which were first tempered in a Silit furnace in undried air. The specimens were removed and weighed after every hour. Heat resistance was determined from the change in weight (increase in weight) in milligrams per square centimeter.

On the basis of the data obtained from thermal, microstructural, and X-ray analyses, the limits of solubility of aluminum and vanadium in niobium were established (Fig. 1, dashed lines on concentration triangle), as were the phase regions and melting points of the alloys at the niobium angle of the ternary diagram for the niobium-vanadium-aluminum system. The melting points are shown as isotherms in Fig. 1. The addition of aluminum to the boundaries of the two-phase regions causes a greater drop in melting point than does the addition of vanadium. The addition of aluminum and vanadium to niobium does not substantially reduce the grain size in the ternary solid solution regions (Fig. 2a, b, c, and d).

The two-phase alloys (Fig. 2e, f) have the typical structure formed in recrystallization by a peritectic reaction and this confirms the data of the previous reference [6].

A region of ternary solid solutions containing up to approximately 3% V by weight is formed on the basis of the compound $Nb_3Al$ (Fig. 2g). It has been established by quenching the alloys at a temperature of $1600^\circ$ that the solubility of vanadium and aluminum in niobium changes little when the temperature is increased.

The hardness of the alloys increases when the quantity of aluminum is increased. Figure 3 shows the hardness curve for a vertical, radial cross section with a V to Al ratio of 1 to 4.

It may be seen from the isoclers of the alloys in Fig. 4 (a horizontal cross section at a temperature of $20^\circ$) that the hardness of the alloys increases more sharply as we move toward the
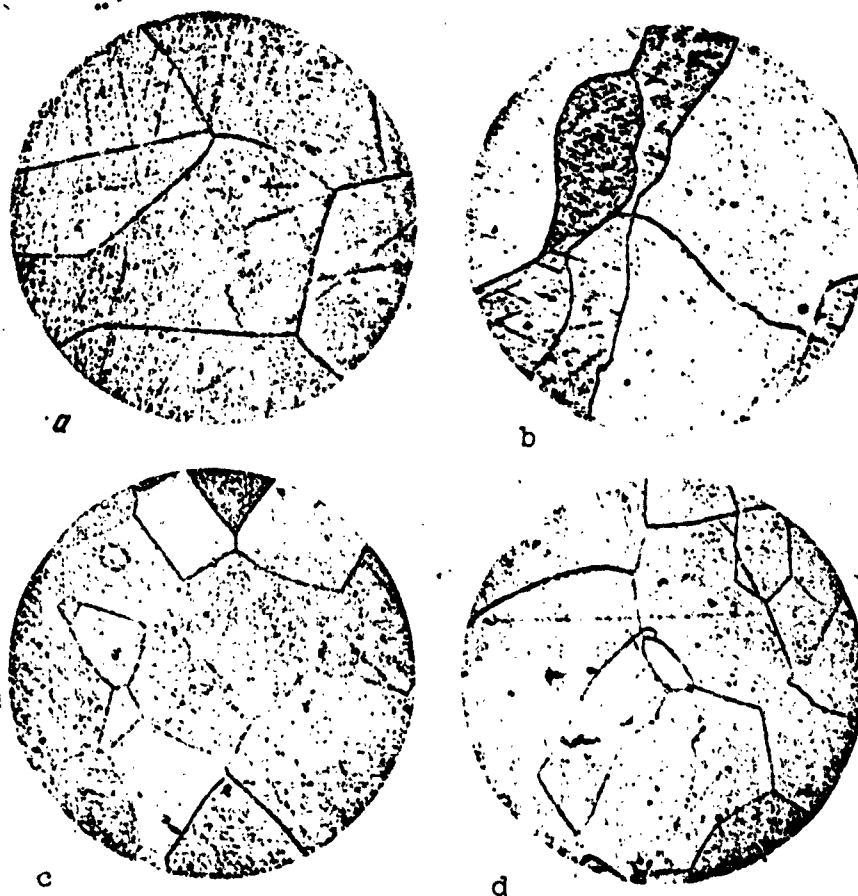
Fig. 2. Structure of alloys in niobium corner
of niobium-vanadium-aluminum phase diagram.
a) Niobium, annealed (200X); b) ternary α-
solid solution, 1.5% V + 0.87% Al (200X);
c) ternary α-solid solution, 2.2% V + 4.76% Al
(200X); d) ternary α-solid solution, 4.0% V +
+ 5.15% Al (200X); (Fig. 2 Cont'd. Page 25);

aluminum side. The addition of vanadium has less influence. The microhardness of the intermetallic compound $Nb_3Al$ is approximately $H_W = 800$ kg/mm$^2$ and changes little when vanadium is added.

Alloys with hardnesses of up to 180 kg/mm$^2$ (the crosshatch region in Fig. 4) were cold rolled into wires 1 mm in diameter, without intermediate annealing. Alloys with hardnesses of up to 250 kg/mm$^2$ were processed at a temperature of 1200°.

Figure 5 shows the rate of oxidation of isothermal cross sections of the alloys at a temperature of 1200°. The alloys rich in
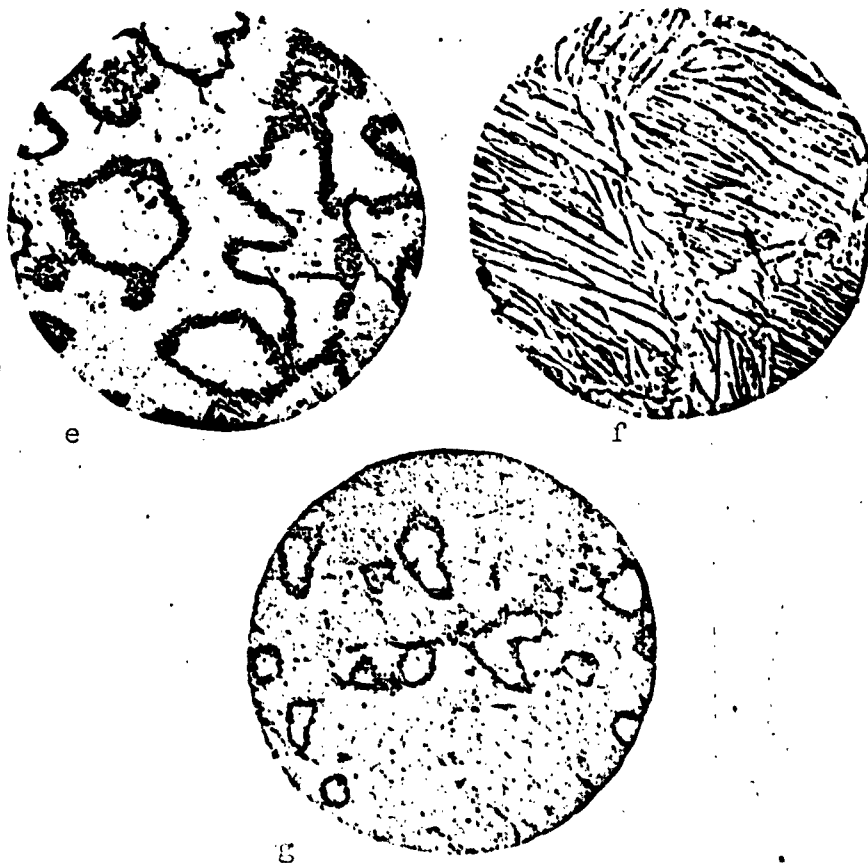
Fig. 2. (Cont'd.) e) ternary α-solid solution + the compound $Nb_3Al$; 1.0% V, 5.4% Al (500X); f) ternary α-solid solution + the compound $Nb_3Al$; 0.5% V, 6.7% Al (500X); g) solid solution based on the compound $Nb_3Al$; 3.0% V, 9.0% Al (500X).

vanadium with an aluminum content of up to approximately 1% have an oxidation rate only 1/5th as great as that of niobium. It may also be seen from Fig. 5 that there are alloys in the aluminum-rich regions whose oxidation rate is only 1/6th that of niobium.

Figure 6a and b shows the weight gain of the alloy specimens as a function of time. The oxidizability of all alloys tested for heat resistance varied linearly, with the exception of alloys rich in aluminum (Fig. 6a, b, curves 6 and 24).

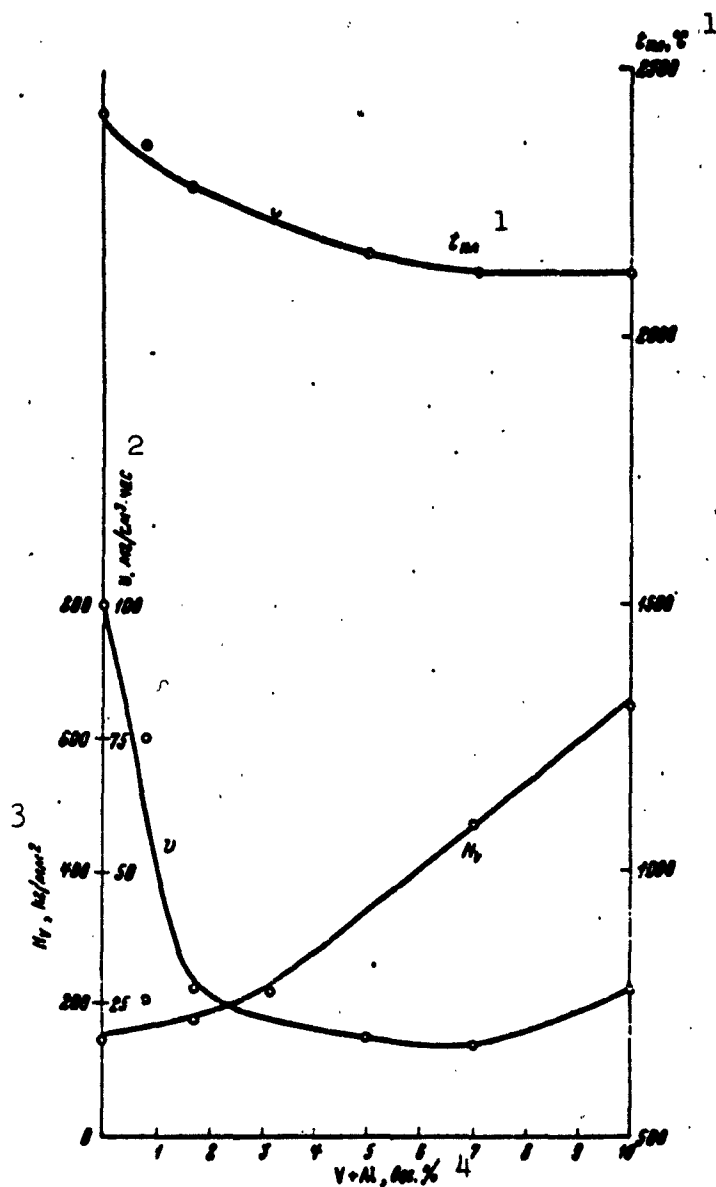A thin brown film, which adheres tightly to the metal, is formed

Fig. 3. Vertical section of niobium corner of
phase diagram of niobium vanadium-aluminum
systems with V to Al ratio of 1 to 4. 1) $T_{pl}$;
2) v, mg/cm$^3$·hr; 3) $H_v$, kg/mm$^2$; 4) V + Al,
% by weight.

in those alloys rich in vanadium. The alloys rich in aluminum have

a characteristic loose, clear film which stands away from the metal.

## CONCLUSIONS

The niobium corner of the ternary diagram of a niobium-vanadium-
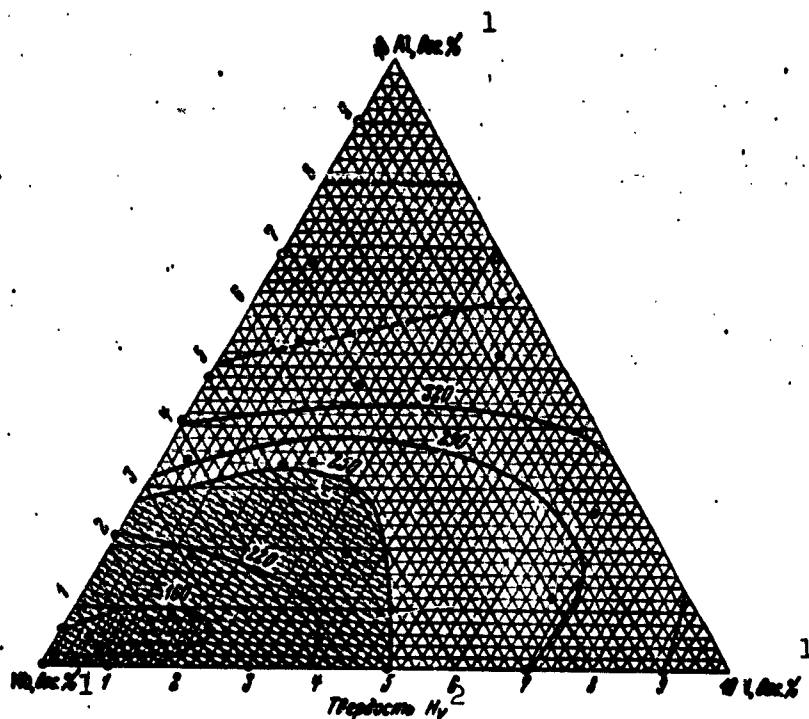aluminum system (containing up to 10% by weight vanadium and alumi-

Fig. 4. Isosclers; horizontal section at 20°.
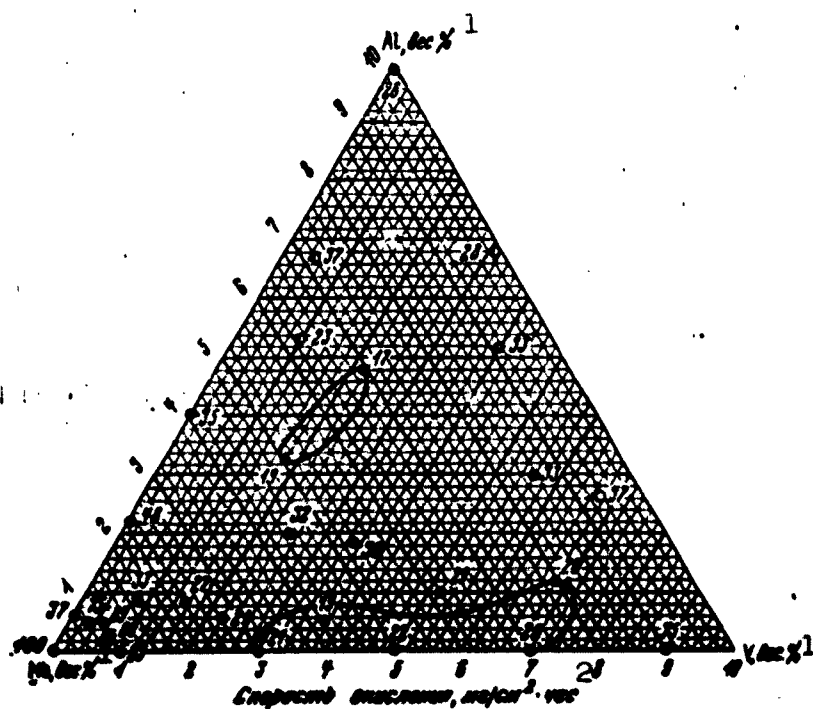1) % by weight; 2) hardness, $H_v$.



Fig. 5. Oxidation rate of alloys in niobium corner
of niobium-vanadium-aluminum diagram, at 1200°.
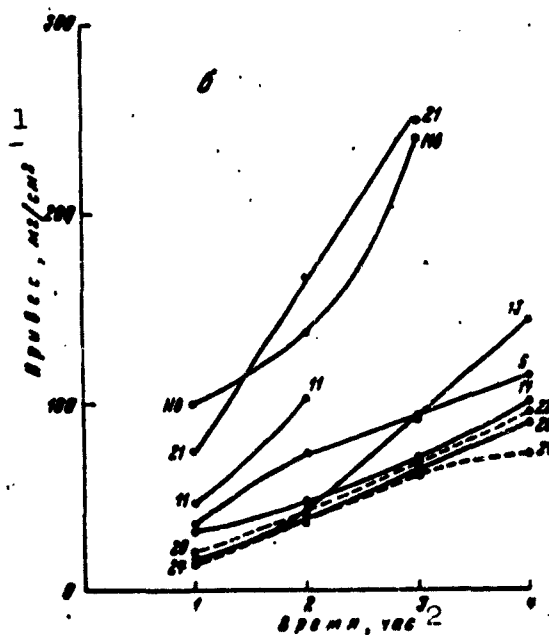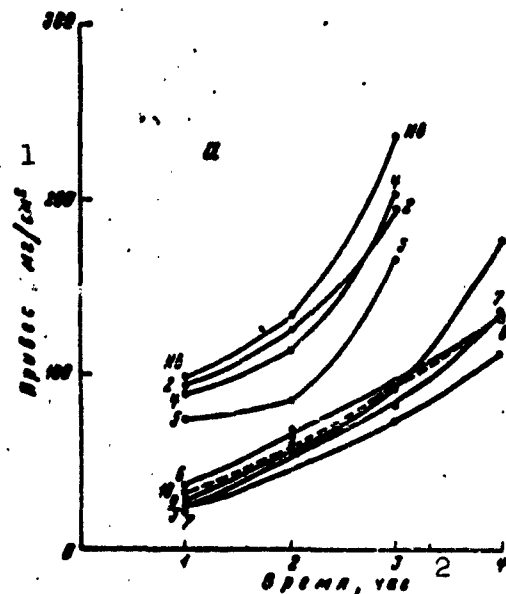1) % by weight; 2) oxidation rate, $mg/cm^2 \cdot hr$.

Fig. 6. Change in oxidation with time for
alloys in the niobium corner of the niobium-
vanadium-aluminum phase diagram, at 1200°.
a) Alloys containing 100-97% Nb; b) alloys
containing 97-91% Nb; 1) gain in weight, $mg/cm^2$;
2) time, hours.

num) has been constructed on the basis of microstructural, thermal,
and X-ray analyses. The presence of a broad region of ternary solid
solutions based on niobium has been established. Vanadium increases
the solubility of aluminum in niobium at room temperature up to 6%

140

aluminum by weight (when the vanadium content is up to 4% by weight).
Alloys in the niobium solid solution region have a high melting
point (above 2100°). As a result of the investigation of the hard-
ness and heat resistance of the ternary alloys, it has been shown
that vanadium and aluminum increase the hardness and heat resistance
of niobium. Alloys containing 3-8% vanadium by weight and approxi-
mately 1.0% aluminum by weight or 1.8-2.2% vanadium by weight and
3.2-4.8% aluminum by weight have the best heat resistance.

Low-alloy niobium alloys (containing up to 1.5% vanadium and
aluminum by weight) are easily processable when cold, with a high
degree of deformation (up to 80%). The hardness of these alloys
does not exceed 175-185 kg/mm$^2$. Alloys with higher vanadium and
aluminum contents (up to 5% vanadium and 2.5% aluminum by weight)
can be processed when heated to a temperature of 1250°.

## REFERENCES

1. H. Wilhelm, O. Carlson, J. Diskinson. Trans. AJME, 1954,
200, 915.

2. W. Rostoker, A. Yamamoto. Trans. ASM, 1954, 46, 1136.

3. R. Elliot. Armour Research Foundation, Chicago, III Tech'n.
Report I, OSR, Techn. Note OSR, 1954, 247.

4. C. Sims, W. Klopp, R. Jaffee. Trans. ASM, 1959, 51, 256.

5. W. Klopp, C. Sims, R. Jaffee. Second International Confer-
ence of the Peacetime Uses of Atomic Energy, held in Geneva, 1958.

6. Ye.M. Savitskiy, V.V. Baron. Neorganicheskaya khimiya [In-
organic Chemistry], Izd-vo AN SSSR [Publishing House of the Academy
of Sciences USSR], 1960.

7. F. Clauss, C. Barret. Technology of Columbium, 1958.

[List of Transliterated Symbols]

Manu-
script
Page
No.

26       пл   = pl = plavleniye = melting

## DISTRIBUTION LIST

| DEPARTMENT OF DEFENSE | Nr. Copies | MAJOR AIR COMMANDS | Nr. Copies |
|---|---|---|---|
| | | AFSC | |
| | | SCFTR | 1 |
| | | ARO | 1 |
| HEADQUARTERS USAF | | ASTIA | 10 |
| | | TD-Bla | 3 |
| AFCIN-3D2 | 1 | TD-Blb | 3 |
| | | AEDC (AEY) | 1 |
| | | TD-B2 | 1 |
| OTHER AGENCIES | | | |
| CIA | 1 | | |
| NSA | 2 | | |
| AID | 2 | | |
| OTS | 2 | | |
| AEC | 2 | | |
| PWS | 1 | | |
| NASA | 1 | | |
| RAND | 1 | | |
| SPECTRUM | 1 | | |
| PWS (GHILARDI) | 1 | | |
| PWS (SNYDER) | 1 | | |