122. E.Swistak, P.Mastagli, and Z.Zafiriadis, Compt.rend., 237, 1713 (1953).
123. S.Yamada, I.Chibata, and R.Tsurui, Pharm.Bull.(Japan), 1, 14 (1953).
124. E.D.Bergmann and R.Corett, J.Org.Chem., 21, 107 (1956).
125. G.E.Underwood and F.E.Deatherage, Science, 115, 95 (1952).
126. M.Astle and R.Etherington, Ind.Eng.Chem., 44, 2871 (1952)
127. P.Mastagli, P.Lambert, and G.François, Bull.Soc.chim. France, 1108 (1957).
128. G.V.Austerweil, Compt.rend., 247, 1726 (1958).
129. J.Remond, Rev.Prod.chim., 63, 417 (1960).
130. O.A.Kolpakov, I.A.Myasnikova, M.A.Barenbaum, N.A. Golitsina, and I.S.Ismailova, Trudy po Khim.i Khim. Tekhnol., Gor'kii, No.3, 701 (1958).
131. R.V.Kucher and V.A.Soroka, Zhur.Prikl.Khim., 34, 1573 (1961).
132. G.A.Razuvaev, V.A.Shushunov, and V.A.Yablokov, Dokl. Akad.Nauk SSSR, 139, 1128 (1961).
133. M.J.Astle and J.A.Oscar, J.Org.Chem., 26, 1713 (1961).
134. L.Alexandru, F.Butaciu, and J.Balint, Rev.Chim.(Acad. R.P.R.), 12, 329 (1961); Translated into Russian in Ekspress-Inform., Ser. "Promyshlennyi Organicheskii Sintez", No.40, 1961, p.19.
135. Kh.R.Rustamov, L.G.Fatkulina, and K.A.Agzyamov, Uzbek.Khim.Zhur., No.2, 32 (1961).
136. S.Imai and I.Khirasaka, Jap.P. 3015 (1960); Ref.Zhur. Khim., I, L 27, 1962, p.399.
137. M.Ya.Klimenko, Z.N.Verkhovskaya, and L.B.Vystavkina, Neftekhimiya, 1, 630 (1961).
138. J.C.Martin and J.P.Hawk, U.S.P.2 972 629 (1961); Ref. Zhur.Khim., 3 L 150, 1962, p.416.
139. B.George and G.Hein, U.S.P.2 904 584 (1959); Ref.Zhur. Khim., I, L 73, 1962, p.373.
140. O.Wright, U.S.P.2 948 759 (1960); Ref.Zhur.Khim., 24 L 162, 1962, p.399.
141. F.Crisp and G.Whitfield, B.P.824 551 (1959); Ref.Zhur. Khim., 24 L 51, 1961, p.379.
142. V.I.Isagulyants and E.V.Panidi, Zhur.Prikl.Khim., 34, 1578 (1961).
143. V.I.Isagulyants and E.V.Panidi, Zhur.Prikl.Khim., 34, 1849 (1961).
144. F.G.Klein and J.T.Banchero, Ind.Eng.Chem., 48, 1278 (1956).
145. P.Mastagli and G.Lagrange, Compt.rend., 248, 254 (1959).
146. N.G.Polyanskii and T.I.Kozlova, Neftekhimiya, 1, 624 (1961).
147. N.G.Polyanskii and E.F.Fedorov, Neftekhimiya, 1, No.6, (1961).
148. N.G.Polyanskii, S.M.Markevich, T.I.Kozlova, and N.L. Potudina, Neftekhimiya, 1, No.6, (1961).
149. V.L.Vaiser, V.D.Ryabov, and B.M.Piryatinskii, Zhur. Prikl.Khim., 34, 1380 (1961).
150. N.G.Polyanskii, Priroda, No.9, 1961, p.95.
151. A.V.Topchiev, V.P.Alaniya, and V.A.Soprano, Dokl. Akad.Nauk SSSR, 139, 396 (1961).

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THE METAL CHEMISTRY OF VANADIUM

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1. METALLIC VANADIUM

Vanadium occurs in Group V of Mendeleev's Periodic System of the elements. Among the metals of industrial importance, vanadium occupies the seventh position, after chromium, in abundance in the Earth's crust, and in this respect considerably surpasses niobium and tantalum, and also molybdenum and tungsten.

The vanadium atom has an unfilled *d* shell, so that vanadium is a transition metal.

The electronegativity series of the metals (according to the "Project for the Nomenclature of Inorganic Compounds" [1]) vanadium occupies an intermediate position, *i.e.* it can be to equal extents an electropositive metal (with respect to metals following it in the electronegativity series) and electronegative (with respect to metals which precede it). This confers on vanadium a special chemical character, and the variety of its chemical compounds is consistent with its position in the electronegativity series of the metals.

Vanadium is among the most difficult of metals to obtain in a pure form. Owing to its great reactivity at high temperatures it gives a series of stable refractory compounds with non-metals. Metallic vanadium is able to absorb considerable quantities of hydrogen. It is only now, when new methods have been developed for preparing vanadium of the highest purity, containing less than 0.05% of impurities, that its physical and mechanical properties can be regarded as firmly established.

Table 1 gives the chemical composition of various grades of vanadium, including both the ductile metal and the brittle, aluminothermic material. To this table should be added the fact that extremely pure vanadium (99.99%) has recently been produced [2] for some new branches of technology. It is prepared in the form of single crystals by the secondary refining of the 99.5% vanadium by methods involving electrolysis, vessel-free zone melting, electron-beam melting, etc. [2]

TABLE 1. Composition of different grades of vanadium (in wt. %).

Element	Grade of vanadium				
	aluminothermic	chloride (metal sponge)	carbothermic	calciothermic	iodide
V	95.37	90.5—99.6	99.73	99.63—99.8	99.88
O	1.54	0.14—0.57	0.045	0.01—0.1	0.012
N	0.066	0.01	0.020	0.005—0.004	0.008
H	0.002	0.001	—	0.005	0.005
C	—	—	0.20	0.12—0.05	—
Si	0.96	—	—	0.04	0.002
Fe	0.78	0.03—0.1	—	0.001—0.05	0.07
Ca	—	—	—	0.001—0.05	—
Mg	—	0.07—0.20	—	—	—
Al	0.61	—	—	0.01	0.05
Cr	—	—	—	—	0.002
Mo	—	—	—	—	0.005

TABLE 2. Principal properties of vanadium.

Crystal structure up to 1550°	body-centred cubic
Lattice constant, Å	3.034
Specific gravity at 20°	5.8
Melting point, °C	1900 ± 25
Heat of fusion, cal $mole^{-1}$	4185
Entropy of fusion, cal g^{-1} deg^{-1}	2.1
Boiling point, °C	3000
Volatility at the melting point	very low
Specific heat at constant pressure over the temperature range 20°–100°, cal g^{-1} deg^{-1}	0.120
Thermal conductivity, cal cm^{-1} sec^{-1}, at 100°	0.074
Ditto at 500°	0.088
Coefficient of linear expansion (200°–1000°)	8.95×10^{-6}
Electrical resistivity at 20°C, Ω cm	26×10^{-5}
Temperature coefficient of resistivity (25°–100°)	28×10^{-3}
Magnetic susceptibility, c.g.s. unit	1.4×10^{-6}
Vickers hardness	
iodide vanadium	70
cold-rolled iodide vanadium	120
calciothermic vanadium	143
Young's modulus, kg mm^{-2}	14 070
Modulus of rigidity, kg mm^{-2}	4730
Tensile strength, σ_b, kg mm^{-2}	22.2
Proportionality limit, kg mm^{-2}	8.5
Proof stress $\sigma_{so.1}$, kg mm^{-2}	10.7
$\sigma_{so.2}$, kg mm^{-2}	11.6

The physical and especially the mechanical properties of vanadium of varying chemical composition have been described in detail[3]. Table 2 gives the chief properties of vanadium of 99.7–99.9% purity.

The plastic properties of pure metallic vanadium are changed markedly even by oxygen contents as low as 0.05% and nitrogen as low as 0.03%. Therefore the ability of a specimen of vanadium to undergo various types of mechanical working may be regarded as a measure of its purity, since appreciable quantities of oxygen, nitrogen, and hydrogen make it an extremely brittle and hard material.

Pure vanadium has low tensile strength, high plasticity, low specific gravity, high corrosion resistance, and a high melting-point, resembling in this respect titanium and zirconium.

2. METAL CHEMISTRY OF VANADIUM

The solution of the problem of the industrial production of pure vanadium in the 1950s and the demands of various branches of industry for new materials enabled a systematic study to be undertaken of the chemical interaction of vanadium with various elements and of the phase equilibria in metallic systems based on vanadium.

The start of this systematic investigation can be regarded as Rostoker's study[4] of the solubility in vanadium of twenty-one elements of the Periodic System, with suggested equilibrium diagrams for several of the systems investigated. Many investigations have been published recently on equilibrium diagrams of binary and ternary systems based on vanadium, in which pure metals were used.

The problem of the interaction of vanadium with other elements can be worked out on the basis of the general laws governing the formation of metallic solutions and intermetallic compounds, established by Hume-Rothery[5], Ageev[6], Kornilov[7], and others. The formation of solid solutions is determined by the following conditions: (1) similarity in the chemical properties of the metals, following from their positions in the Periodic System and in the electronegativity series of the elements; (2) a small difference in atomic radius between the elements, not exceeding 8–10% for the formation of continuous solid solutions, and 14–18% for restricted solid solutions; and (3) isomorphous crystalline structure for the formation of continuous solid solutions.

As the difference in chemical properties between the elements increases, intermetallic compounds are formed until there is a transition from the intermediate type of semiconducting compounds to compounds of ionic type.

TABLE 3. Difference in atomic diameter between vanadium and the other elements of the Periodic System.

Group	Element	Atomic diameter, %*	Difference, %	Group	Element	Atomic diameter, %*	Difference, %
	Subgroup A			8	Fe	2.54	5.5
				8	Co	2.50	7.05
1	H	1.20	55.3	8	Ni	2.49	7.42
1	Li	3.13	16.3	8	Ru	2.67	0.74
1	Na	3.83	42.6	8	Rh	2.68	0.37
1	K	4.76	71.7	8	Pd	2.75	2.22
1	Rb	5.40	100.7	8	Os	2.70	0.37
1	Cs	5.40	100.7	8	Ir	2.71	0.74
				8	Pt	2.88	7.05
2	Be	2.25	16.3		Subgroup B		
2	Mg	3.20	18.9				
2	Ca	3.93	45.9	1	Cu	2.55	5.2
2	Sr	4.29	59.4	1	Ag	2.883	7.05
2	Ba	4.48	66.5	1	Au	2.877	6.7
2	Ra	—	—				
3	B	1.94	27.9	2	Zn	2.748	22.2
3	Al	2.80	4.08	2	Cd	3.042	13.1
3	Sc	3.02	12.2	2	Hg	3.10	15.2
3	Y	3.62	34.6				
				3	Ga	2.74	1.86
4	Ti	2.93	8.2	3	In	3.138	16.6
4	Zr	3.19	18.8	3	Tl	3.427	27.4
4	Hf	3.17	17.8				
4	Th	3.60	33.8	4	C	1.54	42.8
				4	Si	2.34	13.01
5	V	2.69	—	4	Ge	2.78	3.3
5	Nb	2.94	9.3	4	Sn	3.168	17.8
5	Ta	2.94	9.3	4	Pb	3.494	29.8
6	Cr	2.57	4.46				
6	Mo	2.80	4.08	5	N	1.42	47.2
6	W	2.82	4.82	5	P	2.20	18.2
6	U	2.81	4.46	5	As	2.80	4.08
				5	Sb	3.228	2.0
7	Mn	2.60	3.3	5	Bi	3.640	35.2
7	Re	2.75	2.2				

* *Sic.* It is not clear whether kX or Å is intended. For accepted atomic diameters the reader may consult W. Hume-Rothery, "Elements of Structural Metallurgy", Institute of Metals Monograph and Report Series No. 26, 1961, pp. 38–39 (Ed. of Translation).

Work on the laws governing the formation of intermetallic compounds has been surveyed[8].

The above conditions for the formation of solid solutions and intermetallic compounds have been verified many times in connection with the solubility of elements in iron, nickel, chromium, and titanium[7,9-12]. These same generalisations can be applied to the study of the formation of solid solutions and compounds of vanadium.

Table 3 gives the difference in atomic diameter between vanadium and elements arranged according to their position in the Periodic System. These data are important in determining the nature of the interaction between vanadium and the other elements. Below we shall examine published data on the interaction of vanadium with other elements in the order of their position in the Periodic System.

3 INTERACTION WITH ELEMENTS OF GROUP I

Data are available on the interaction of vanadium only with hydrogen, copper, silver, and gold. The interaction of vanadium with hydrogen has been discussed in a monograph by Mikheeva on the hydrides of the transition metals[13].

Since the absorption of hydrogen greatly increases the hardness of vanadium, several authors have suggested that a solid solution of hydrogen in vanadium is formed, but what type of solid solution is obtained is unknown. Absorbed hydrogen can be removed from the metal by heating in a vacuum to 400°. This indicates the instability of vanadium hydrides as chemical compounds. A vanadium hydride containing 38.6–50 at.% of hydrogen is obtained[14] by reducing V_2O_3 with calcium hydride in a stream of hydrogen at 1175° for 45 min. This hydride is dark grey to black. It was first discovered by Hägg in a study of the adsorption of hydrogen by vanadium on heating[15]. The adverse effect of hydrogen on the physicochemical and mechanical properties of vanadium is noteworthy.

The alkali metals differ greatly from vanadium in chemical properties and in atomic diameter. Therefore vanadium should not interact with them, apart, perhaps, from lithium. It is because they do not interact with vanadium that alkali metals can be used to reduce its compounds and to obtain pure vanadium uncontaminated by these elements

Metals of the copper subgroup (Cu, Ag, Au) are characterised by completion of the *d* electron shell and have a smaller tendency to give solid solutions with metals of the transition groups, including vanadium

Copper forms with vanadium a restricted series of solid solutions. Rostoker and Yamamoto[4] consider the limiting solubility of copper in vanadium to be 5.5–8 at.%. In the copper–vanadium equilibrium diagram it is suggested that a region of liquid immiscibility exists between 20 and 80 wt.% of copper, but these data must be regarded only as tentative[16]. For silver there are only isolated data on the mutual insolubility of the metals in both liquid and solid states[4].

The gold–vanadium equilibrium diagram has been published recently[17] (Fig. 1): the solubility of gold in vanadium is 19 at.% at 1520° and 8 at.% at room temperature. A peritectic reaction between the melt and the α solid solution of gold in vanadium at 1520° yields the compound V_3Au (24 at.% Au), which has a small range of homogeneity. At

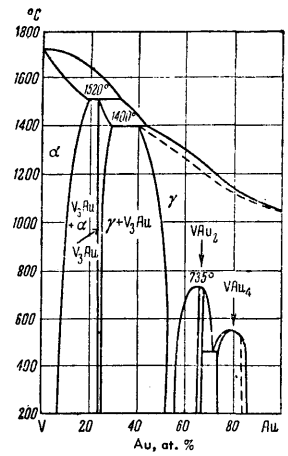


Fig. 1. Equilibrium diagram of the gold–vanadium system.

1400° a solid solution of vanadium in gold is formed by the peritectic reaction:

$$L + V_3Au \rightleftharpoons \gamma\dagger.$$

The gold concentrations in the phases are then: *L* 44, V_3Au 28, and γ 41 at.%. The solubility of vanadium in gold is 59 at.% at 1200°, and 48 at.% at room temperature.

As the temperature falls the γ solid solution yields two intermetallic compounds of Kurnakov type, V_3Au_2 and VAu_4, which are formed at 735° and 565° respectively. Both compounds have regions of homogeneity, and coexist in the eutectoid equilibrium at 460°. The region of the diagram within which both phases exist lies between 56 and 85 at.% gold. VAu_4 has the $MoNi_4$ type of structure with a = 6.39 kX and c/a = 0.622. The structure of VAu_2 has not been established. V_3Au is isomorphous with V_3Co, V_3Ni, and V_3Pd, its lattice constant being 4.87 kX.

4. INTERACTION WITH ELEMENTS OF GROUP II

Group II metals of subgroup A, like the alkali metals, differ considerably from vanadium in chemical properties and atomic diameter, and therefore they should not form solid solutions with it. Beryllium is an exception (the difference in atomic diameter being 16.3%). The limiting solubility of beryllium in vanadium is 0.8 wt.% (4.3 at.%). The equilibrium diagram of the beryllium–vanadium system[4] is of eutectic type, the eutectic point being at Be 49.9 at.%, 1680°. X-Ray examination of this system has revealed a VBe_2 phase, isomorphous with $MgZn_2$ and possessing a hexagonal structure, and a phase VBe_{12}, which belongs to the $ThMn_{12}$ type[18].

Since magnesium and calcium do not interact with vanadium their use is widespread in the development of methods for obtaining vanadium from its compounds such as chlorides, oxides, and sulphides.

The interaction of vanadium with Group IIB elements (zinc, cadmium, and mercury) is not discussed in the literature. In view of the considerable difference in atomic

† Here and subsequently, *L* = liquid phase.

diameter and the great difference in melting point and boiling point, it is difficult to suppose that they can interact with vanadium to form solutions and compounds.

5. INTERACTION WITH ELEMENTS OF GROUP III

Among the elements of subgroup A in Group III, boron, which has a small atomic diameter, is able to yield very dilute solid solutions with vanadium, and to form with it a series of metallic compounds, the borides. The solubility of boron in vanadium does not exceed 2 at.%.[4] Rostoker and Yamamoto have confirmed by X-ray diffraction the existence of the vanadium borides VB (17.52 wt.% B) and VB_2 (29.81 wt.%). VB has an orthorhombic lattice of the CrB type, and is apparently formed[4] by a peritectic reaction between VB_2 and the melt at 1780°. VB_2 has a hexagonal structure and is isomorphous with other diborides (Ti, Zr, Nb, Ta)B_2. Such borides as V_2B_5 (isomorphous with Ti_2B_5, W_2B_5, and Cr_2B_5)[19] and V_3B_4 [20] are known.

A tentative equilibrium diagram for the boron–vanadium system has been suggested recently (Fig. 2)[21]. The starting materials were vanadium containing < 0.5% impurities and boron powder containing B 96, Mg 0.9, Fe 0.14, Si 0.1%, and a considerable amount of oxygen. Alloys were prepared from the powders by sintering under pressure in argon at 1600° for 12 h, and by normal sintering in argon in a tubular tungsten furnace at 1800° for 4 h. Under such treatment the alloys rich in vanadium and those rich in boron melted.

The presence in the vanadium–boron system of the previously known borides VB, V_3B_4, and VB_2 has been confirmed by means of X-rays, and a new compound V_3B_2 has been found. However, the existence of the previously reported compound V_2B_5 was not proved, either in the sintered or in the cast specimens. The concentration range of the homogeneous regions of these borides was not established by the X-ray examination, but it is assumed to be small. Melting-point determinations using a micropyrometer and studies of the microstructure indicate that the compounds V_3B_2, VB, and VB_2 melt without decomposition, whereas V_3B_4 is formed by a peritectic reaction. The eutectic reaction

$$L \rightleftharpoons V_3B_2 + \alpha$$

takes place at 1550° and 15 at.% B. The position of the

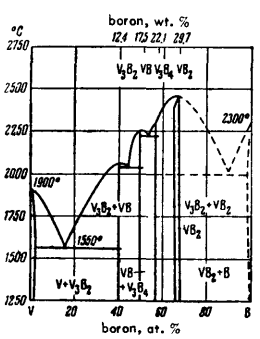


Fig. 2. Tentative equilibrium diagram for the boron–vanadium system.

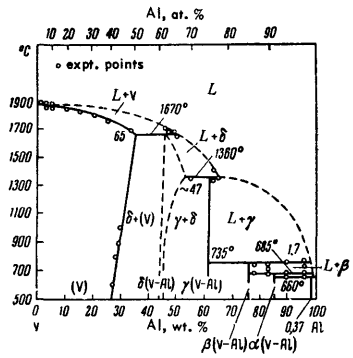


Fig. 3. Equilibrium diagram of the aluminium–vanadium system.

second eutectic, adjacent to the opposite side of the diagram, has not been determined exactly. Methods for preparing the various vanadium borides and their properties have been reviewed[22].

The aluminium–vanadium equilibrium diagram is shown in Fig. 3. The alloys were prepared from ductile vanadium obtained by reduction with calcium. In contrast to Rostoker and Yamamoto's work, in which alloys containing up to 70 wt.% vanadium were studied, later workers[23] investigated thoroughly the whole system, and made additions and corrections to the equilibrium diagrams suggested previously. Thus a new δ phase was discovered, which is formed by a peritectic reaction between the liquid phase and vanadium solid solution at 1670°. It contains 54.2 wt.% (38.5 at.%) vanadium, corresponding to the formula V_5Al_8. This is the only phase which has a wide homogeneity range. Two other phases, γ (VAl_3), melting at 1360°, and β (VAl_6), which melts incongruently at 735°, were described earlier by Rostoker and Yamamoto. They were the first to detect the β phase. A peritectic reaction between the liquid and the β phase at 658° yields a new α phase, which can be given the composition VAl_{11} (14.6 wt.% or 8.3 at.% V). It can also be regarded as a solid solution of VAl_{10} and V_2Al_{21}. The solubility of vanadium in aluminium is low, 0.37 wt.% (0.19 at.%) at 660°. Neither the formation of a compound by a peritectic reaction at 1215°, which had been suggested by Rostoker and Yamamoto, nor the existence of such phases as V_2Al, VAl, V_2Al_3, VAl_7, and VAl_4 could be confirmed[23]. The crystal structure of an α′ phase in an alloy containing 2.5 wt.% aluminium has been studied[24]. The parameters of the monoclinic α′ phase are $a = 25.604 \pm 0.014$, $b = 7.6213 \pm 0.0018$, $c = 11.081 \pm 0.012$ Å, and $\beta = 128°55'$. The composition of the α′ phase was found to be V_7Al_{45} from the density and the volume of the unit cell. Positions are given for all the atoms, together with the interatomic distances and the coordination, and the similarity in structure between the α′ phase and the α and β phases is noted.

The equilibrium diagrams for the systems formed by vanadium with the remaining elements of Group III of the Periodic System, including the lanthanides, are unknown. The fact that pure vanadium is obtained by reducing V_2O_5 with a mixture of lanthanides indicates that these metals do not form appreciable ranges of solid solutions with vanadium. Recently an investigation has been made of the

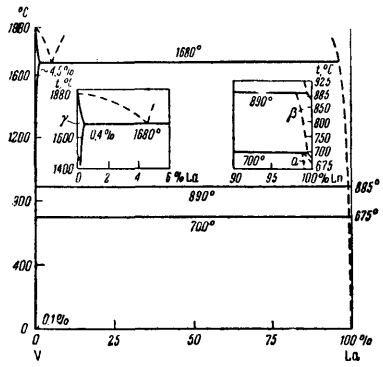


Fig. 4. Equilibrium diagram of the lanthanum–vanadium system.

interaction of vanadium with lanthanum[25]. The alloys were made from carbothermic vanadium (99.3% V) and from lanthanum of purity 98.5% in an arc furnace in an atmosphere of helium (0.5 atm) by remelting four times. Fig. 4 shows the equilibrium diagram for the lanthanum–vanadium system. This diagram has a broad miscibility gap in liquid and solid states. The microstructure of alloys containing 4–99.5% lanthanum showed the presence of two layers, γ rich in vanadium and α rich in lanthanum. Alloys containing $<4\%$ or $>99.5\%$ lanthanum have a two-phase structure. Lanthanum and vanadium form restricted solid solutions. The solubility limit of lanthanum in vanadium is 0.1% at 20°, and 0.47% at 1650°. The solubility of vanadium in α- and β-lanthanum is $<0.5\%$, and also increases with rise in temperature.

Addition of lanthanum to vanadium causes a marked depression of the melting-point of the latter to 1680°, which is a monotectic temperature. At 890° the peritectic reaction $L + \gamma \rightleftharpoons \beta$ results in formation of the β solid solution based on lanthanum. Vanadium raises the polymorphic transformation temperature of lanthanum, a solid solution based on α-La being formed at 700° by the peritectoid reaction $\gamma + \beta \rightleftharpoons \alpha$. The ease of oxidation of alloys containing $>0.5\%$ lanthanum was noted.

Vanadium does not form solid solutions with elements of the IIIB subgroup (gallium, indium, and thallium), in conformity with the difference in chemical properties and the ratio of their atomic diameters. The properties of the intermetallic compound V_3Ga have been described[90]. At 17°K it is superconducting. There is evidence that at 0°K the critical magnetic field of this compound may reach more than 500 000 oersteds.

6. INTERACTION WITH ELEMENTS OF GROUP IV

The elements of subgroup A in Group IV (titanium and zirconium) interact with vanadium to form solid solutions. The nearest neighbour to vanadium in the Periodic System, titanium, has a similar atomic diameter, and at high temperatures its lattice (β modification) is isomorphous with that of vanadium. Hence in this modification it should form a continuous series of solid solutions on crystallisation with vanadium. The equilibrium diagram of the titanium–vanadium system has been thoroughly studied[26,27]. The version in Fig. 5 is based on Adenstedt *et al.*[26] The liquidus has a minimum at 31 at.% V. Vanadium markedly lowers the polymorphic transformation temperature of titanium, and consequently the area of the α phase region is small. The $\alpha + \beta$ two-phase region extends at 650° to 21 at.% vanadium. This equilibrium diagram[26] has been confirmed by other work[4,27], the differences amounting merely to a somewhat different solubility of vanadium in α-titanium.

Titanium–vanadium alloys containing 15–17 wt.% V undergo marked precipitation hardening, which increases appreciably the hardness, diminishes the plasticity, and produces a considerable change in the lattice constant[28].

The X-ray photograph of a titanium–16% vanadium single crystal which had been aged at 460° for 30 min showed reflections due to a new ω phase, the unit cell of which can be assigned to the hexagonal system with constants of $a = 4.60$ Å and $c = 2.82$ Å. The ω phase is a metastable phase. A study has been made of the kinetics of its formation in alloys containing 15 and 17.5 wt.% vanadium[29]. After homogenising in the β region (900°–950°) the specimens were quenched in water, and then maintained at temperatures of 200° to 700°. During this treatment, the ω phase was precipitated. Brief heating of the aged alloys at temperatures above 550° results in almost complete dissolution of the ω phase. When the specimens are maintained a second time at lower temperatures, the ω phase is formed afresh, in smaller amount the longer the specimen had been previously maintained at the temperature of dissolution of the ω phase.

The variation of the modulus of elasticity and of the internal friction with composition of quenched and annealed titanium–vanadium alloys has been investigated[30]. The starting materials were vanadium of 99.5% purity and sponge titanium having $H_B = 130$ kg mm^{-2}.

Fig. 6 shows the concentration dependence of the modulus of elasticity and the internal friction of the alloys at room temperature. Analysis of the curves indicates that the minimum value of the former and the maximum value of the latter for quenched alloys are located in the region of the martensitic α phase, while the maximum Young's modulus occurs within the range of the β phase. The critical concentration for stabilisation of the β phase is 14.5 wt.%

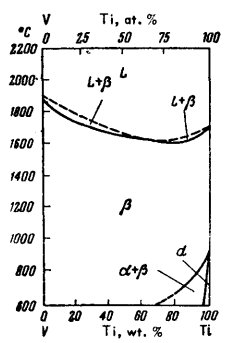


Fig. 5. Equilibrium diagram of titanium–vanadium system.

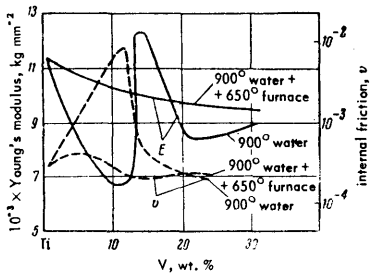


Fig. 6. Variation in Young's modulus E and in internal friction v with composition of titanium–vanadium alloys.

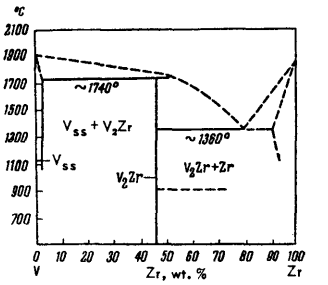


Fig. 7. Equilibrium diagram of the vanadium–zirconium system.

of vanadium[30]. From a study of the temperature dependence of the modulus of elasticity it has been concluded[30] that, with titanium–vanadium alloys having the β structure, the first step in the formation of the ω phase takes place below 280°, the ω phase is formed above 280°, and the equilibrium phase separates above 500°.

With zirconium, vanadium forms restricted solid solutions, in conformity with the great difference in atomic diameter. The limiting solubility of zirconium is less than 1.7 at.% at 1000°, and still smaller at room temperature. Fig. 7 reproduces the equilibrium diagram of the vanadium–zirconium system[4]. Although vanadium and titanium do not form any compounds, the vanadium–zirconium system yields the compound ZrV_2, which is formed by a peritectic reaction between the vanadium solid solution and the melt at 1740°. This compound is in eutectic equilibrium at 1360° with the zirconium solid solution.

No information is available in the literature on the interaction of vanadium with hafnium. From the ratio of the atomic diameters it can be supposed that hafnium, as the closest congener of zirconium,, will give extremely restricted series of solid solution with vanadium. For the same reasons thorium should not dissolve at all in vanadium in the solid state. The vanadium–thorium equilibrium diagram[31] in Fig. 8 shows a simple eutectic type of system. The eutectic is located at V ~ 19 at.%, 1400°.

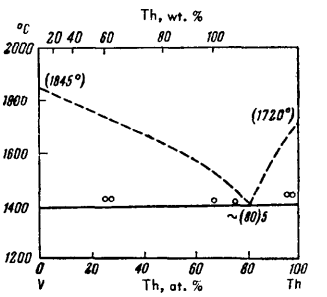


Fig. 8. Equilibrium diagram of the thorium–vanadium system.

Carbon and silicon interact with vanadium to form extremely restricted solid solutions and a series of compounds, of the carbide and silicide types.

Owing to the great difference in atomic diameter, carbon forms extremely restricted solid solutions with vanadium[32,33]. The small atomic diameter of carbon results in the formation, as in its interaction with iron, of solid solutions of interstitial type. According to Schönberg[33], the solubility of carbon in vanadium is 0.2 wt.% (1 at.%) at 1000°.

Much work has been done on the carbide phases of vanadium, and this has been critically reviewed[3,34]. The equilibrium in the carbon–vanadium system has been investigated[4] up to 19 wt.% carbon, the proposed diagram being reproduced in Fig. 9. Schönberg used 99.7% vanadium for preparing vanadium–carbon alloys and reported two carbide phases, V_2C and VC. The hexagonal V_2C phase had a homogeneity range of 8–10.5 wt.% (27–33 at.%). The VC phase had the homogeneity range of 15.1–18.5 wt.% (43–49 at.%) carbon.

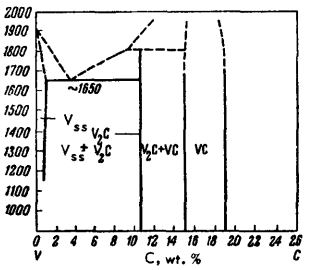


Fig. 9. Equilibrium diagram of the carbon–vanadium system.

Gurevich and Ormont[35] studied the structure of the carbide phases of vanadium containing up to 18 wt.% carbon and 0.14 wt.% oxygen. They concluded that the carbide phases, whatever their mode of preparation, contained a certain amount of oxygen in the form of oxide carbides. Apart from the known carbides V_2C and VC, which these workers[35] regard as oxide carbides, a new phase was discovered having a homogeneity range roughly from $VC_{0.5}O_{0-0.1}$ to $VC_{0.7}O_{0-0.14}$ and a face-centred cubic lattice with constants of 4.115–4.130 kX. The existence of such phases as V_2C and V_4C, which Osawa and Oya[36] found in this system, has been denied[4,34,35].

The solubility of silicon in vanadium is less than 5 wt.% (6.4 at.%) close to the melting point of vanadium, and less than 2.5 wt.% (3 at.%) at 900°. The eutectic reaction

$$L \rightleftharpoons V_{ss} + V_3Si$$

is said[4] to take place in vanadium–silicon melts on the vanadium side at 1840°. A study of the microstructure of the cast alloys showed that, at temperatures above 2000°, a peritectic reaction takes place between the liquid phase and V_3Si with the formation of a new phase, the composition of which was not determined and was tentatively assumed to be VSi. X-Ray structural analysis has established[37] the lattice type and the composition of the unknown silicide, which corresponds to the formula V_5Si_3 and is isomorphous with Ta_5Si_3, β-Nb_5Si_3, Cr_5Si_3, Mo_5Si_3, and W_5Si_3. Kieffer *et al.*[38] confirmed this structure and composition, and gave the silicon–vanadium equilibrium diagram shown in Fig. 10.

A series of papers on silicide systems by the Austrian scientist Nowotny[37,39] are of great value in the search for extra-hard heat-resistant materials. All the vanadium silicides shown on the silicon–vanadium equilibrium diagram were prepared, and the systems formed by the silicides were studied.

Table 4 summarises Nowotny's results on the nature of the interaction between vanadium silicides and those of other metals.

The VSi_2–$TiSi_2$ system has been studied in greater detail[40]. Fig. 11 shows the variation in the physical properties of such alloys, which are very heat-resistant. Their addition to other alloys, which readily oxidise on heating, considerably increases the heat-resistance of the latter.

Table 5 gives the chief properties of the vanadium silicides[34,38,40,41].

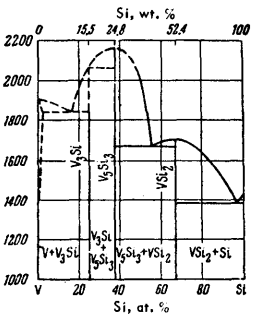


Fig. 10. Equilibrium diagram of the silicon–vanadium system.

TABLE 4.

VSi_2			V_5Si_3		V_3Si	
continuous solid solutions	restricted solid solutions	minimum solubility	continuous solid solutions	restricted solid solutions	continuous solid solutions	restricted solid solutions
$NbSi_2$	$TiSi_2$ $MoSi_2$	$ZrSi_2$	Ta_5Si_3 Nb_5Si_3	Zr_5Si_3	Cr_3Si Mo_3Si	— —

In the vanadium–germanium system, alloys containing 29–83% of vanadium have been studied by X-ray microstructural methods[42]. Apart from the known germanide V_3Ge, which belongs to the Cr_3Si structural type[43], the existence of a new compound V_5Ge_3 was established[42], this having a structure of the $MnSi_3$ type (a = 7.270 kX, c = = 4.960 kX, c/a = 0.676). In rapidly cooled alloys this

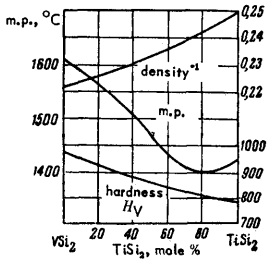


Fig. 11. Variation of physical properties in the VSi_2–$TiSi_2$ system.

TABLE 5. Principal properties of vanadium silicides.

Property	Silicides		
	V_3Si	V_5Si_3	VSi_2
Silicon content, %	15.5	24.8	52.4
Structure	cubic	tetragonal	hexagonal
Lattice constants, kX			
a, Å	4.712	9.41	4.562
c, Å	–	4.74	6.359
c/a	–	0.504	1.394
Density (experimental), g cm^{-3}	5.67	4.80	4.71
Microhardness (100 g load) kg mm^{-2}	1430–1560	1350–1510	1090
Melting point, °C	1730	2150	1670
Electrical resistivity (25°), $\mu\Omega$ cm	–	–	9.5
Temperature of transformation to superconducting state, °K	17.0	–	–
Change in weight on oxidation, kg cm^{-2}, at 1250°	63.0	–7.7	+25
at 1400°	–	–600	–12
Standard heat of formation, ΔH°_{298}, kcal mole^{-1}	–27±9	–96±46	–75±21

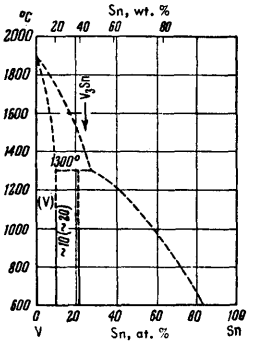


Fig. 12. Tentative equilibrium diagram for the tin–vanadium system.

compound is in equilibrium with germanium and with the compound V_3Ge. Formation of a solid solution of germanium in vanadium is possible on the basis of the ratio of their atomic diameters.

Fig. 12 shows a tentative equilibrium diagram for the tin–vanadium system[44] based on X-ray and microstructural examination of ten alloys which had been annealed at various temperatures up to 1100°. The maximum solubility of tin in vanadium (α solid solution) is approximately 20 wt.% (10 at.%). The compound V_3Sn (47.71 wt.% Sn) has a cubic lattice with the constant[45] a = 4.94 Å, and is formed by the peritectic reaction:

$$L + \alpha \rightleftharpoons V_3Sn.$$

There is no reference in the literature to the interaction of vanadium with lead. From the ratio of the atomic diameters it would appear that solid solutions would not be formed in this system.

7. INTERACTION WITH ELEMENTS OF GROUP V

Niobium and tantalum, Group VA elements, are direct analogues of vanadium, having an isomorphous crystal structure and a small difference in atomic diameter compared with vanadium. It is this which governs their interaction with the latter metal.

One of us predicted, during an investigation of the formation of continuous series of solid solutions of the transition metals, the formation of such solutions of vanadium with niobium and with tantalum[12]. Later experimental work on vanadium alloys containing up to 70 wt.% niobium[4] supported this prediction. Alloys in the neighbourhood of 36 at.% niobium showed, after being annealed at 900°, some signs of a transformation in the solid state. This was ascribed[4] to the formation of a σ phase, which is very characteristic of alloys of transition metals. Later any hypothesis of intermediate phase formation in the niobium–vanadium system was rejected, and an equilibrium diagram with a continuous series of solid solutions was proposed (Fig. 13)[46]. The liquidus curve is characterised by a minimum at 1810° and 35 wt.% niobium.

A study has been made[47] of the heat-resistance, mechanical properties, and corrosion in boiling aqueous media of alloys of vanadium containing 20–50 wt.% niobium. Fig. 14 shows that the addition of niobium to vanadium greatly increases the corrosion resistance in boiling H_2SO_4 and HNO_3. In moist chlorine at room temperature such alloys corrode at a rate of 25 μ per annum. The alloy containing 50% niobium is the most corrosion resistant in all the media examined.

Table 6 shows that alloys based on vanadium possess inadequate resistance to oxidation during prolonged service in air above 700°, although additions of niobium suppress the formation of liquid oxides. However, the relatively simple alloys containing 60% of vanadium and 40% of niobium show such a high corrosion resistance at high temperatures that they are fully able to compete with the best industrial alloys based on iron or nickel, especially if the comparison is made on the basis of specific strength.

A study has been made[4] of alloys containing up to 80 wt.% tantalum, which in the cast state consist solely of solid solution. Alloys within the range 25–80 wt.% tantalum, after being annealed at 900°, contain a second phase, which on the basis of the X-ray diffraction pattern, is ascribed[4] to the family of σ phases.

In an investigation[48] of the structure and properties of tantalum–vanadium alloys undertaken with the aim of constructing the equilibrium diagram of the system, the initial vanadium contained Al 0.5, Fe 0.22%, and an appreciable quantity of oxygen. The alloys were prepared in an arc

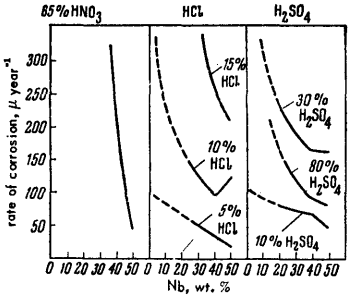


Fig. 14. Corrosion resistance of vanadium–niobium alloys in boiling media.

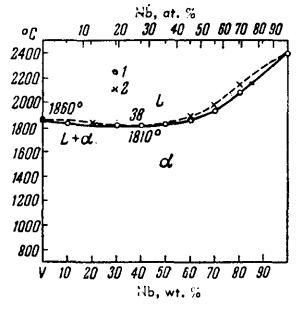


Fig. 13. Equilibrium diagram of the niobium–vanadium system: 1) end of crystallisation; 2) start of crystallisation.

TABLE 6. Corrosion and mechanical properties of vanadium–niobium alloys.

Composition, wt.%	Equilibrium rate of oxidation, mg cm^{-2} h^{-1}			Tensile strength, σ, kg mm^{-2}			Proof stress, $\sigma_{0.2}$, kg mm^{-2}			Elongation, %		
	700°	800°	900°	room temp.	700°	1000°	room temp.	700°	1000°	room temp.	700°	1000°
70 V 30 Nb	14,4	32.6*	—	brittle fracture	88.9	—	—	63.7	—	—	24	—
60 V 40 Nb	9.8	57.4	64.0*	brittle fracture	71.6	24.4	—	63	21.6	—	7.4	8
50 V 50 Nb	8.7	312.0	510.0*	—	—	—	—	—	—	—	—	—

* Some liquid phase observed.

furnace in an atmosphere of argon, the beads being remelted six or seven times in view of the great difference in melting point and density between the components. Alloys containing up to 50 at.% Ta were annealed at 1600°, and those containing more than 50 at.% Ta at 1800° for 3 h. The results (Fig. 15) confirm the formation of a continuous series of solid solutions between vanadium and tantalum. When alloys containing 32.04 and 41.5 at.% Ta were annealed at 1400°, the solid solution broke down with the precipitation of a small quantity of a new phase; as the temperature was lowered the region of breakdown of the solid solution became wider. No conclusions were reached[48] concerning the nature of the new phase. Other workers[49] have found on the melting-point diagram a minimum at Ta 30%, 1820° and also an intermediate β phase (TaV_2, 63.9% Ta), which is formed below 1320°. The two-phase $\alpha + \beta$ region covers the range 27.5–87.5% Ta at 900°.

The elements of subgroup B in Group V differ markedly in chemical properties from vanadium. Whereas the metal congeners in Group V tend to form continuous solid solutions, the elements in subgroup B tend to the same extent to give various kinds of compounds, without appreciable ranges of solid solutions.

The solubility of nitrogen in vanadium is very limited[4]. An alloy containing 1 wt.% (2.9 at.%) nitrogen has a single-phase structure when as-cast, but after being annealed at 900° it has a two-phase structure. Higher nitrogen contents yield vanadium nitride VN, which, like oxides, carbides, and nitrides of other metals, has the sodium chloride structure. The homogeneity range of vanadium nitride is 37.8–49.4 at.% nitrogen, and its melting point is ~2050°.[50]

A new vanadium nitride V_3N has been discovered[50] with a hexagonal structure and a homogeneity range of 27.1–29.9 at.% nitrogen. It can be prepared[51] by heating a mixture of stoichiometric amounts of VN and vanadium powder, compressed into tablets under high pressures, in well evacuated quartz tubes at 1000°–1100° for 24 h.

Powdered vanadium nitrides are greyish brown with a bronze tinge, and are chemically stable, VN more so than V_3N.

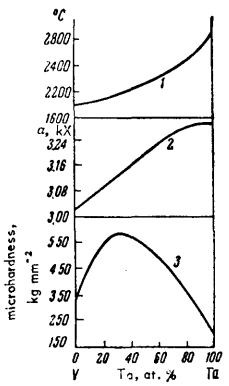


Fig. 15. Property–composition curves of vanadium–tantalum alloys: 1) temperature of crystallisation; 2) lattice constant; 3) microhardness.

Vanadium forms a series of phosphides VP_2, VP, and $VP_{<1}$ (several phases on the phosphorus–vanadium equilibrium diagram)[52]. The most stable among them is VP, which is stable up to 1057°. VP_2 can be obtained from the elements with excess of phosphorus, and VP is obtained by the decomposition of VP_2 in a vacuum at 700°–900°. The vanadium phosphides are dark grey substances, the lower phosphides having a semi-metallic lustre and being resistant to acids. The structure of VP_2 is like that of NbP_2 and TaP_2, and V_3P resembles Cr_3P and $(Fe, Co, W)_3P$ in structure.

The arsenic–vanadium and antimony–vanadium equilibrium diagrams have not been investigated systematically. Nowotny *et al.*[53] suggest that vanadium forms more than one compound with arsenic. They obtained VAs by heating the elements in an evacuated quartz vessel. It dissociates in a vacuum above 1000° to V_2As, which melts at 1345°. They also obtained the compound VSb_2, which is isomorphous with $CuAl_2$.

No information is available in the literature on the interaction of vanadium with bismuth.

8. INTERACTION WITH ELEMENTS OF GROUP VI

Among the elements in subgroup A, chromium and molybdenum form continuous solid solutions with vanadium. This is fully consistent with the conditions stated above for the formation of such solutions, and agrees with the predictions made by one of us[12]. No transformations have been observed in the chromium–vanadium system in the solid state[4,54,55].

The complete equilibrium diagram for the chromium–vanadium system has been published recently[56]. The original vanadium contained Al 1, Fe 0.15, C 0.2, Si 0.35%, and an appreciable quantity of oxygen, the latter affecting the properties of the binary alloys. Addition of the second component has comparatively little effect on the melting point of the alloys, all those in the middle of the diagram melting at ~1700° (Fig. 16). Several properties (hardness and electrical resistivity), however, vary greatly with composition (Fig. 16), the character of the change and the microstructure of the alloys indicating complete solubility of vanadium and chromium in the solid state. The presence of impurities in the vanadium does not prevent complete miscibility of the components; it only raises considerably the hardness and the resistivity, and displaces the maximum in the properties towards vanadium.

The magnetic susceptibility of a solid solution of vanadium and chromium has been studied[57] with the aim of determining its fine structure.

Fig. 17 shows the variation in density, hardness, and magnetic susceptibility with the composition of the alloys. The hardness of alloys prepared from pure materials increases from 90 H_V for pure vanadium to 400 H_V for alloys containing 50% chromium. The hardness of alloys prepared from less pure metals lies about 150 units above the basic curve. The comparatively broad maximum on the magnetic susceptibility curve at 50% chromium is ascribed to the formation of a Kurnakov type of compound, the time for ordering of the solid solution being less than a few seconds. However, no superlattice lines were observed on the X-ray photographs, and if ordering does take place, it occurs to the extent of less than 10%. This phenomenon is quite possible, since vanadium and chromium atoms have

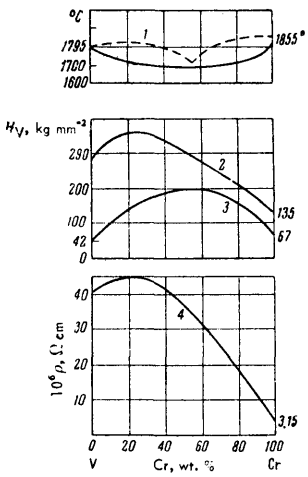


Fig.16. Equilibrium diagram and properties of chromium–vanadium alloys: 1) fusion diagram; 2) hardness in annealed condition; 3) hardness at 1000°; 4) electrical resistivity at 25°.

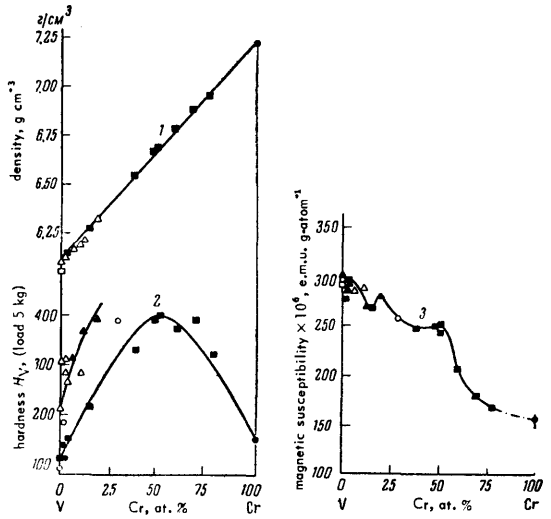


Fig.17. Variation of properties with composition of chromium–vanadium alloys: 1) density; 2) hardness; 3) magnetic susceptibility.

closely similar electrochemical properties and dimensions. The presence of a fine structure in this region has been shown in other work, involving neutron diffraction and specific heat measurements. Fig. 18 shows the molybdenum–vanadium equilibrium diagram with complete miscibility of the components in liquid and solid states[58]. The alloys were prepared from aluminothermic vanadium of 95.5% purity and 99% molybdenum by fusion in an electric arc in argon. Before the properties of the alloy were determined, it was annealed in a vacuum at 1600° for 10 h.

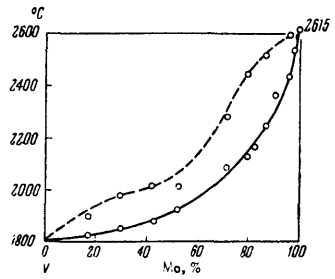


Fig.18. Fusion diagram of the molybdenum–vanadium system.

It is evident from Figs. 19 and 20 that addition of the second component markedly increases the hardness, microhardness, and resistivity of the alloys while diminishing their plasticity.

A vanadium–tungsten equilibrium diagram has been suggested[59,60] which shows complete mutual solubility of the components. Addition of tungsten to vanadium, and especially of vanadium to tungsten, lowers the melting point, the liquidus passing through a minimum at W 4.5 at.%, 1430°.

Apart from determinations of the liquidus and solidus temperatures, several properties of the alloys were studied[60] as a function of their composition (Fig. 21). The alloys were prepared from carbothermic vanadium (98.6%) and from tungsten rods (99.95%) in an arc furnace in an atmosphere of helium, and then annealed at 1100° for 500 h. Additions of tungsten up to 1.25 at.% decrease the hardness and increase the plasticity and compressive strength. The subsequent property–composition curves are typical of systems having unlimited solubility of the components. The alloys oxidised readily in air, and the attack increased progressively with rise in temperature and in the vanadium content of the alloys. It was concluded[60] that at 700°–1000° all the alloys oxidise vigorously, and require protection.

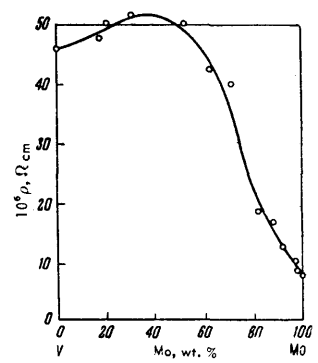


Fig.19. Variation in resistivity in the molybdenum–vanadium system.

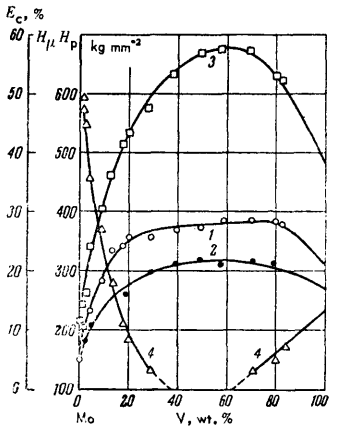


Fig. 20. Variation in mechanical properties in the molybdenum–vanadium system: 1) hardness of as-cast alloys (H_p); 2) hardness of annealed alloys; 3) microhardness (H_μ); 4) plasticity on compression (ϵ_c).

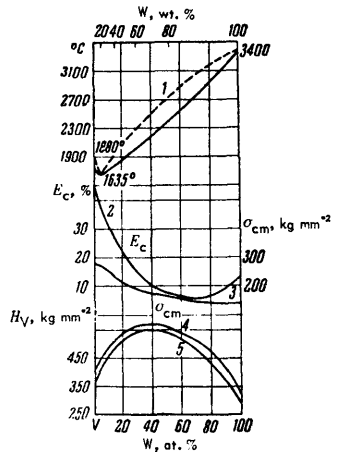


Fig. 21. Equilibrium diagram and properties of tungsten–vanadium alloys: 1) fusion diagram; 2) and 3) plasticity and compressive strength; 4) hardness of as-cast alloys; 5) hardness of annealed alloys.

The equilibrium diagram for the uranium-vanadium system[61] is illustrated in Fig. 22. The alloys were prepared in an electric arc furnace in helium from iodide vanadium and the purest uranium containing at most 0.1% of impurities. The equilibrium diagram is of eutectic type, the eutectic point being at V 18 at.%, 1040°. The temperatures of the allotropic transformations in uranium are lowered by vanadium. The solubility of vanadium in γ-uranium is 12 at.% at the eutectic temperature, falling to 9 at.% at the eutectoid temperature (727°). The solubility of vanadium in the β modification is 2 at.% at 700°, that in the α modification being 1.5 at.% at 600°. The solubility of uranium in vanadium (δ phase) is a maximum at the eutectic temperature, its value being 4 at.% or 15 wt.% uranium.

The equilibrium diagram of the plutonium–vanadium system has recently become known[62]. It is of simple eutectic type (Fig. 23), the eutectic point occurring at V 2.3 at.%, 625°. Additions of vanadium do not affect the polymorphic transformation temperature of plutonium.

The interaction of vanadium with the Group VIB elements, oxygen, sulphur, and their congeners, results in the formation of a series of compounds which have been thoroughly investigated and well described. No data are available on the interaction of vanadium with polonium.

The equilibrium diagram of the oxygen–vanadium system has been studied repeatedly and thoroughly as a result of its great practical importance. The early work, concerned

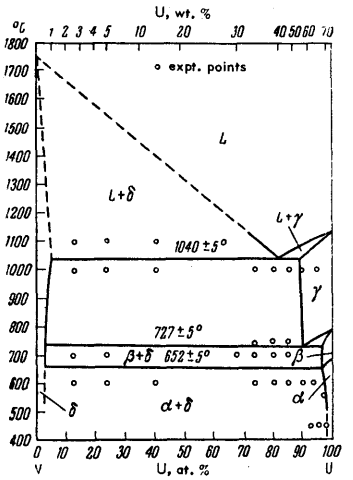


Fig. 22. Equilibrium diagram of the uranium–vanadium system.

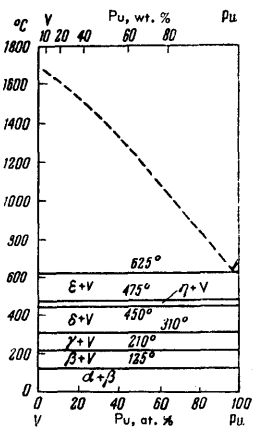


Fig. 23. Equilibrium diagram of the plutonium–vanadium system.

mainly with the oxides of vanadium VO, V_2O_3, VO_2, and V_2O_5, their crystal structure, and the conditions and limits of their existence, has been reviewed by Pearson[63]. Seybolt and Sumsion[64] have established that vanadium undergoes a high-temperature polymorphic transformation at 1500°, and this is reflected in the equilibrium diagram which they proposed for the V–VO_3 system (Fig. 24).

Up to 3.2 at.% oxygen is dissolved by α-vanadium, and up to 35–40 at.% by the high-temperature γ modification. A later paper[65] denies the existence of a high-temperature modification of vanadium, and gives a different V–VO equilibrium diagram (Fig. 25). The alloys were prepared from calciothermic vanadium (total impurities 0.13%) and chemically pure V_2O_5 in an arc furnace. The limiting solubility of oxygen in α-vanadium at temperatures below 900° was found to lie between 0.27 and 0.98 at.%. At 1600° the maximum solubility reaches 3.9 at.%. X-Ray examination has established that at room temperature a β phase, with a body-centred tetragonal lattice, exists over the range 8–40 at.% oxygen. This phase is regarded[65] as a low-temperature allotropic modification of vanadium which is stable at high temperatures in the oxygen–vanadium system.

The $(\alpha + \beta)/\beta$ phase boundary passes from 14.5 at.% oxygen at 900° to 22.1 at.% at 1800°, in agreement with Seybolt and Sumsion's results. Below 1100° a δ phase, the crystal structure of which was not determined, is formed by a peritectoid reaction between the β phase and VO. Between 41 and 56 at.% oxygen is the region of homogeneity of the compound VO, which has the NaCl structure with a lattice constant of a = 4.08 kX.

Investigations were made not only of transformations in the solid state but also of the fusion diagram, which showed a minimum at 30.2 at.% oxygen[65], agreeing with the minimum on the diagram based on Seybolt and Sumsion's data. At the temperature of the minimum it is the β phase which solidifies, not the γ phase as the latter investigators imagined. Over the range 0–50 at.% oxygen the fusion diagram contains two peritectic horizontals on the two sides of the minimum, at the temperatures of which the following reactions take place:

$$L + \alpha \rightleftharpoons \beta\ (1850°) \quad \text{and} \quad L + VO \rightleftharpoons \beta\ (1690°).$$

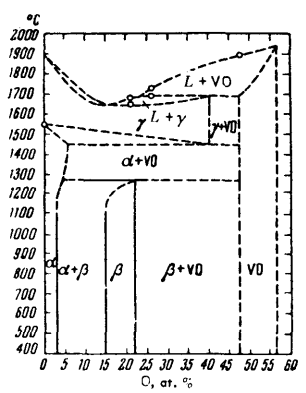


Fig. 24. Equilibrium diagram of the V–VO system according to Seybolt and Sumsion.

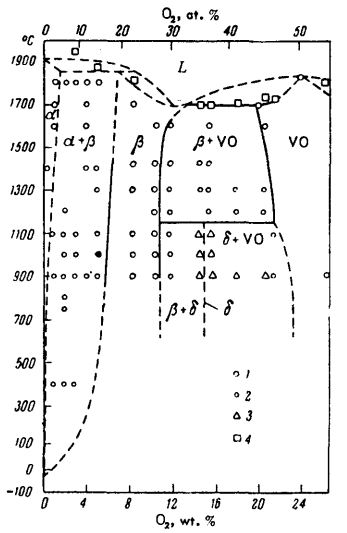


Fig. 25. Equilibrium diagram of the V–VO system according to Rostoker: 1) one phase; 2) two phases; 3) three phases; 4) thermal analysis.

In order to confirm their hypothesis of a low-temperature allotropic modification of vanadium, Rostoker and Yamamoto[65] measured the electrical resistance of a fine vanadium wire as a function of temperature in a vessel containing dry ice and acetone. The curve (Fig. 26) shows a change in resistivity (a break) between -33° and -25°.

Oxygen tends to stabilise the β modification, which has a considerable range of homogeneity in the oxygen–vanadium system. However, doubt has been cast[66] on the existence of a low-temperature modification of vanadium. The curve for the temperature dependence of the electrical resistance of cold-worked vanadium wires containing 99.7 and 99.9% vanadium showed[66] no breaks which would indicate first-order transitions; it is characterised merely by a slight negative deviation from linearity at 73°. The curve representing the temperature dependence of Young's modulus of the vanadium wire showed neither a break nor a deviation from linearity. X-Ray examination indicated only a body-centred cubic lattice.

The following phases have been established[67] in the sulphur–vanadium system: an α phase VS, which is in eutectic equilibrium with vanadium at 1312° and has a nickel arsenide type of structure, a β phase V_2S_3 with an asymmetric structure, and VS_4, which is stable in the presence of sulphur up to 400°. The existence of the previously discovered sulphide V_2S_5 has been denied[67].

A study of the crystal structure of the sulphide richest in vanadium, V_3S, has shown[68] that it exists as two polymorphic modifications, β-V_3S stable above 950°, and α-V_3S stable below 825°; interconversion of these two sulphides occurs between these temperatures. β-V_3S has a body-centred tetragonal structure with lattice constants of a = 9.470 and c = 4.589 Å; α-V_3S has a tetragonal structure with constants a = 9.881 and c = 4.663 Å. The structure of β-V_3S is similar to the Ni_3P type, and the α-V_3S structure is close to that of β-W. A complete crystallographic description of these two forms of V_3S is given.

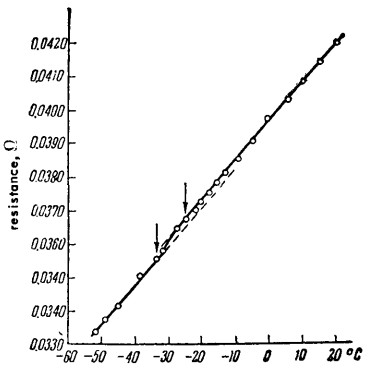


Fig.26. Change in electrical resistance of vanadium wire between -33° and -25°.

The equilibrium diagrams selenium–vanadium and sulphur–vanadium systems are similar in general character[63]. The following phases have been shown by means of X-rays[69] to be present in the selenium–vanadium system: VSe isomorphous with NiAs, V_2Se_3 with a hexagonal lattice of low symmetry, and VSe_2 isomorphous with CdI_2.

The only vanadium telluride known as yet is VTe, which is isomorphous with NiAs[70].

9. INTERACTION WITH ELEMENTS OF GROUP VII

The equilibrium diagrams of vanadium with the metals of Group VII have not been fully studied. Formation of a continuous series of solid solutions between manganese and vanadium is excluded since the crystal structures of the components are not isomorphous and manganese exists in several polymorphic modifications. In conformity, however, with the very slight difference in atomic diameter between the components, manganese shows considerable solubility in vanadium, the limit of which has still not been reached[4] in the alloy containing 14.2 at.% manganese at 900°. The equiatomic alloy has a body-centred cubic structure, and is regarded[71] as an intermetallic compound of vanadium with manganese having the composition VMn.

Manganese-rich alloys contain a σ phase, whose range of homogeneity at 1000° is 13.4–24.5 at.% vanadium[72].

The literature contains a hint of the existence of the compound VMn_2 (33.3 at.% vanadium), melting at 1370°. An alloy having the composition VMn_2 which has been cast and annealed at 1300° and 1200° has a body-centred cubic structure, while those which have been annealed at 1000°, 800°, and 600° are mixtures of two phases, one having a body-centred cubic structure and the other a σ phase structure[31].

Vanadium and rhenium have a slight difference in atomic diameter, which favours the formation of a considerable range of solid solutions, which may contain[73] up to 40 at.% vanadium. No intermetallic compounds have been detected within the range 40–68 at.% vanadium.

It has been established[74] that a σ phase of the composition VRe_3 is formed in the rhenium–vanadium system by a peritectic reaction at 2490° between the melt and the solid solution based on rhenium. The results of X-ray and microstructural analyses indicated the occurrence of a eutectoid breakdown of the σ phase at 1500° with the formation of a mixture of two solid solutions, based on vanadium (α) and on rhenium (β). The lattice constants of the phase are a = 9.36 and c = 4.86 Å.

No data are available on the interaction of vanadium with technetium.

With the halogens, vanadium forms halides of the types $VHal_2$, $VHal_3$, and $VHal_4$. The chlorides and iodides are important as raw materials in the industrial production of pure vanadium.

10. INTERACTION WITH ELEMENTS OF GROUP VIII

Vanadium should interact with all the Group VIII elements to form solid solutions and compounds containing a metallic type of bond. Of the nine elements in this group, equilibrium diagrams are known only for the systems with iron[54,75,76], cobalt[77], nickel[4,72,78], and palladium[79].

With iron, vanadium forms a continuous series of solid solutions, in conformity with the general conditions governing the formation of such solid solutions between metals.

Fig. 27 reproducts the equilibrium diagram for the iron–vanadium system given in Hansen's Handbook[31]. When the α solid solution is cooled, a Kurnakov compound VFe,[76] which dissolves both iron and vanadium, is formed at 1230°. The range of homogeneity of this compound, the σ phase, lies between 37 and 57 at.% vanadium. The plots of hardness and of resistivity against composition for alloys which have been annealed at 900° for 70 h pass through singular minima at 25 and at 50 at.% vanadium, corresponding to the compounds VFe_3 and VFe respectively[80,81]. The binary iron–vanadium system contains a closed region of a face-centred γ solid solution, with a maximum at 1.2 at.% vanadium.

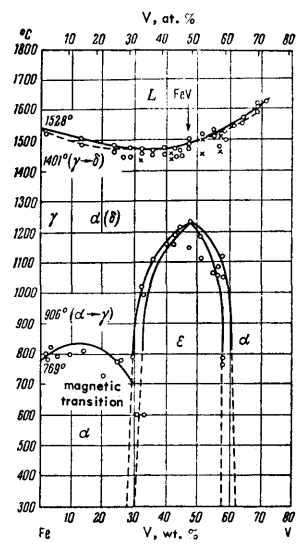


Fig.27. Equilibrium diagram of the iron–vanadium system.

With certain conditions of heat treatment, a second ferromagnetic phase is formed in an iron alloy containing 47% vanadium. High-temperature annealing at 1360° for 60 h with subsequent quenching in alkali is of decisive value in this connection.

A study has been made[83] of the structure of iron alloys containing 28.5, 43.0, 49.5, and 74.0 at.% vanadium, after they have been heated at various temperatures between 1400° and 600° with subsequent quenching in water. All alloys in the temperature range 1400°–1150°consist of a mixture of two phases ($\alpha+\beta$). The second phase, the face-centred cubic β-Fe–V, is regarded[83] as the equilibrium phase in the temperature range above the $\alpha \rightleftharpoons \sigma$ transformation, its amount increasing with increase in the vanadium content. At 800° the alloy containing 28.5% vanadium consists of a single phase, α, whereas alloys containing 43, 49.5, and 74% vanadium consist of two phases, α and σ. At 600° crystals of the α phase disappear from the alloy containing 49.5% vanadium, and its structure consists solely of the σ phase. It is therefore considered[83] that the phase reactions occurring within the range 28.5–74 at.% vanadium when the temperature is lowered from 1400° to 600° are more complicated than would appear from the published iron–vanadium equilibrium diagram.

The analogues of iron — cobalt and nickel — show greater differences from vanadium in atomic diameter, and are not isomorphous with it in crystal structure. This explains the gap in the solubility of cobalt and nickel in vanadium. According to data in the literature[77], the solubility of cobalt in vanadium is 20 at.% at high temperatures and 5% at room temperature.

The equilibrium diagram of the vanadium–cobalt system[77] is shown in Fig. 28. At the eutectic temperature of 1248° the melt is in equilibrium with γ and σ phases, the latter being formed at 1420° by a peritectic reaction between the melt and the vanadium solid solution. The homogeneity region of the solid solution (σ phase) based on the compound VCo lies between 38.5 and 59.5 at.% vanadium[67].

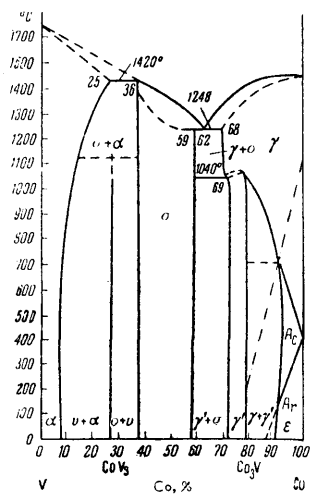


Fig. 28. Equilibrium diagram of the cobalt–vanadium system.

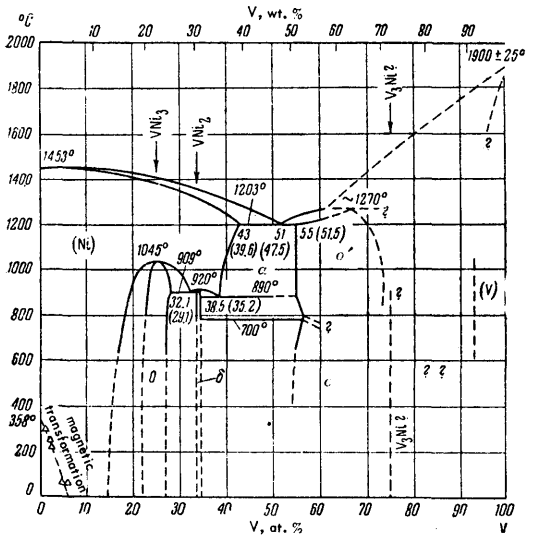


Fig. 29. Equilibrium diagram of the nickel–vanadium system.

An alloy containing 70.7 at.% vanadium undergoes, at temperatures between 1100° and 1150°, a eutectoid reaction between the α and σ phases with the formation of the metallic compound V_3Co, which crystallises with the β-tungsten structure. In the region of the cobalt solid solution at 1070°[84] a new ordered γ' phase based on the compound VCo_3 (a Kurnakov compound) is formed with a homogeneity range of 19.1–26.09 at.% vanadium, on both sides of which are two-phase regions, $\gamma+\gamma'$ and $\gamma'+\sigma$. The X-ray photograph of the ordered phase shows weak superstructural lines. It has a close-packed hexagonal structure containing 24 atoms in the unit cell with lattice constants of a = = 5.032 and c = 12.27 kX.[85]

The solubility of nickel in vanadium is 6–9 at.%.[4] Fig. 29 shows the equilibrium diagram of the nickel–vanadium system[77] up to 60% vanadium. At the eutectic temperature a solid solution of vanadium in nickel, the α phase, is in equilibrium with the σ' phase, which has a considerable range of homogeneity, from 55 to 74 at.% vanadium, and at 760° undergoes the transformation $\sigma' \rightarrow \sigma$, the nature of which is not yet known. X-Ray studies do not distinguish between the σ and σ' phase. The $\alpha/(\alpha+\sigma)$ and $(\alpha+\sigma')/\sigma$ boundaries have been established by means of X-ray studies. At 840° the eutectoid decomposition $\alpha \rightleftharpoons \delta + \sigma'$ takes place, and at 907° $\alpha \rightleftharpoons \theta + \delta$. The δ phase, which has a body-centred orthorhombic lattice, is a solid solution based on the compound VNi_2 (30.27 wt.% vanadium). The θ phase, which has a tetragonal lattice of the $TiAl_3$ type, is a solid solution based on the compound VNi_3, the latter being formed at 1045°.

There are indications[4,86] of the formation of the compound V_3Ni (72.25 wt.% vanadium), having the β-W structure, by a peritectic reaction in the vanadium-rich region at 1380°.

Only restricted solid solutions and intermetallic compounds can be formed between vanadium and the platinum

group elements owing to the absence of isomorphism between the crystal structures. Alloys of vanadium with palladium have been most fully investigated [73,79], while those of vanadium with ruthenium, rhodium, and platinum have been studied to some extent [73]. There is no published information on the interaction of vanadium with osmium or iridium.

The palladium–vanadium equilibrium diagram is of eutectic type (Fig. 30). At the eutectic temperature of 1340° an α solid solution of palladium in vanadium, containing up to 37.5 at.% palladium at this temperature, is in equilibrium with a γ solid solution of vanadium in palladium. At 840° a peritectoid reaction yields the compound V_3Pd having the β-W structure with a = 4.80 kX, isomorphous with V_3Ni. This compound has a narrow range of homogeneity, and has no plasticity. In the region of the γ solid solution the ordering process involves the formation of two intermetallic compounds: VPd_3 at 815°, with a face-centred tetragonal lattice having the parameters a = 3.84, c = 3.87 kX, and c/a = 1.007, isomorphous with VNi_3; and VPd_2 at 905°, with a similar lattice having a = 3.88, c = 3.72 kX, and c/a = 0.962. The eutectoid reaction

$$\gamma \rightleftharpoons VPd_3 + VPd_2$$

occurs at V 28 at.%, 720°. At room temperature the γ phase is homogeneous not only up to 21 at.% vanadium but also between 44 and 50%. The solubility of palladium in vanadium at 500° is 15 at.%.

No definite data are available on the solubility of ruthenium in vanadium. Alloys containing 36, 50, 71, and 82 at.% ruthenium, after being quenched from 1200°, have been studied [73] by means of X-ray diffraction. The 36% Ru alloy has a cubic lattice of the CsCl type with a lattice constant which is very close to that of the solid solution based on vanadium. A phase having a tetragonal lattice was found in the 50% alloy. The solid solution of vanadium in ruthenium contains less than 18 at.% vanadium [73]. The same paper [73] reports an investigation of alloys containing 25, 42, 50, and 60 at.% rhodium after being quenched from 1200°. The compound V_3Rh (42.24 wt.% rhodium), having the β-W type of crystal lattice, has been detected. The alloy containing 60 at.% rhodium contains a second compound having a close-packed hexagonal structure.

The limiting solubility of platinum in vanadium [45] is 8 at.% (25 wt.%), and the solubility of vanadium in platinum is 40 at.%. [73] The compound V_3Pt (43.91 wt.% vanadium), isomorphous with V_3Pd, has been found. A further compound may exist between the platinum-rich solid solution and V_3Pt. [73]

11. TABLE SHOWING INTERACTION OF ELEMENTS OF THE PERIODIC SYSTEM WITH VANADIUM

The theoretical concepts and experimental results discussed enable us to give a general picture of the nature of the chemical interaction of vanadium with all the elements in the Periodic System. By analogy with other metals which we have examined previously [87-89], the interaction of the elements with vanadium can be represented in terms of Mendeleev's Periodic Table. This is shown in Fig. 31 in extended form, vanadium being place above the Table.

The elements can be divided into four classes in relation to vanadium: (1) those forming continuous solid solutions with vanadium; (2) those forming restricted solid solutions and intermetallic compounds; (3) those forming ionic compounds but no solid solutions; and (4) those which do not interact with vanadium.

In Fig. 31, which we shall call the "Table of the Metal Chemical Properties of Vanadium", these classes are separated from one another as shown, and are linked by straight lines with vanadium. It can be accepted that metals which are close to vanadium in the Periodic System will form solid solutions with it. Most of them tend to give intermetallic compounds, which are formed either as a result of reaction in the solid solutions or, as in the case

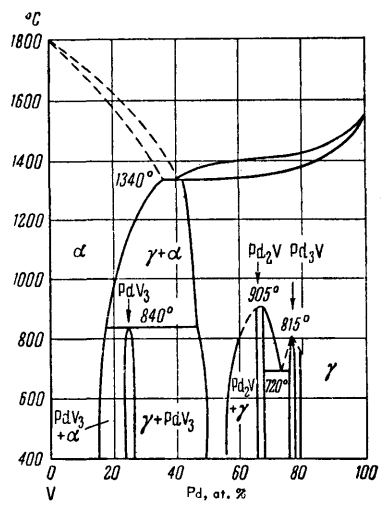


Fig. 30. Equilibrium diagram of the palladium–vanadium system.

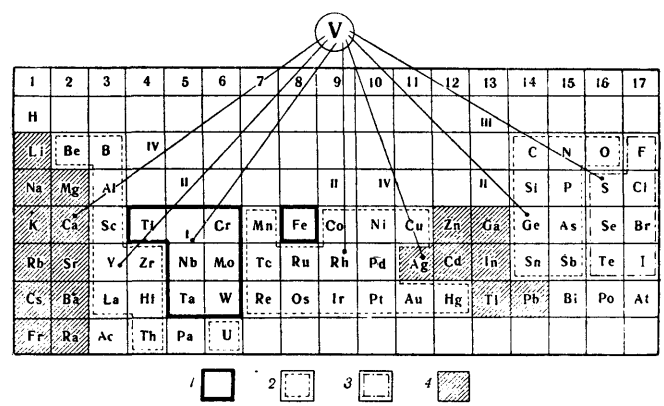


Fig. 31. Metal chemical table of the elements: 1) continuous solid solutions; 2) restricted solid solutions and intermetallic compounds; 3) ionic compounds without solid solutions; 4) no interaction.

of systems having limited solid solutions, directly on crystallisation. Such non-metals as H, B, C, Si, N, and O, which have small atomic diameters, form with vanadium extremely restricted solid solutions of the interstitial or substitutional types. They show a greater tendency to form compounds of the type of the borides, carbides, silicides, nitrides, and oxides of vanadium. With increasing difference in electronic structure and in chemical properties, the tendency to form solid solutions diminishes. With elements which differ markedly in chemical properties, vanadium is unable to give solid solutions, but forms compounds of ionic type. The last class comprises those elements which, owing to an unfavourable size factor or electronic structure, are incapable of interacting with vanadium. It includes the alkali and the alkali-earth metals and, perhaps, several other metals (Zn, Cd, Pb, etc.).

1. "Proekt Nomenklatury Neorganicheskikh Soedinenii, Dolozhennyi na 8 Mendeleevskom S'ezde po Obshchei i Prikladnoi Khimii" (Proposal for the Nomenclature of Inorganic Compounds, presented at the Eighth Mendeleev Conference on General and Applied Chemistry), Izd. Akad. Nauk SSSR, 1939.
2. D.D. Blue and D.H. Baker, "Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958" Paper USA, 15/p/698.
3. W. Rostoker, "The Metallurgy of Vanadium", Wiley, New York, 1958.
4. W. Rostoker and A. Yamamoto, Trans. Amer. Soc. Metals, 46, 1136 (1954).
5. W. Hume-Rothery, "The Structure of Metals and Alloys" (Translated into Russian), GONTI, 1938.
6. N.V. Ageev, Izv. Sektora Fiz. Khim. Anal., Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR, 8, 175 (1938).
7. I.I. Kornilov, "Zheleznye Splavy" (Iron Alloys), Vol. 2, Izd. Akad. Nauk SSSR, 1951.
8. I.I. Kornilov and B.K. Vul'f, Uspekhi Khim., 28, 1086 (1959).
9. I.I. Kornilov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 475 (1950).
10. I.I. Kornilov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 980 (1953).
11. I.I. Kornilov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 392 (1954).
12. I.I. Kornilov, Dokl. Akad. Nauk SSSR, 73, 495 (1950).
13. V.I. Mikheeva, "Gidridy Perekhodnykh Metallov" (The Hydrides of the Transition Metals), Izd. Akad. Nauk SSSR, 1960.
14. G.A. Meierson, G.A. Kats, and A.V. Khokhlova, Zhur. Prikl. Khim., 13, 1770 (1940).
15. H. Hägg, Z. phys. Chem. [B], 11, 444 (1931).
16. J.R. Keeler (Editor), "The Reactor Handbook, Vol. 3, Materials" (Translated into Russian), Inostr. Lit., Moscow, 1956.
17. W. Köster and H. Nordskog, Z. Metallk., 51, 501 (1960).
18. A. Zalkin, G.E. Sands, R.G. Bedford, and O.H. Krikorian, Acta Cryst., 14, 63 (1961).
19. P. Schwarzkopf and F.W. Glaser, Z. Metallk., 44, 353 (1953).
20. D. Moskowitz, Trans. AIME, 206, 1525 (1956).
21. H. Nowotny, F. Benesovsky, and R. Kieffer, Z. Metallk., 50, 258 (1959).
22. G.V. Samsonov, L.Ya. Markovskii, A.F. Zhigach, and M.G. Valyashko, "Bor, Ego Soedineniya i Splavy" (Boron, Its Compounds and Alloys), Izd. Akad. Nauk Ukrain. SSR, Kiev, 1960.
23. O.N. Carlson, D.J. Kenney, and H.A. Wilhelm, Trans. Amer. Soc. Metals, 47, 520 (1955).
24. P. Brown, Acta Cryst., 12, 995 (1959).
25. E.M. Savitskii, V.V. Baron, and Yu.V. Efimov, Trudy Inst. Metallurgii Akad. Nauk SSSR, No.V, 166 (1960).
26. H.K. Adenstedt, J.R. Pequignot, and J.M. Raymer, Trans. Amer. Soc. Metals, 44, 990 (1952).
27. P. Pietrokowsky and P. Duwez, Trans. AIME, 194, 627 (1952).
28. F.R. Brotzen, E.L. Harmon, and A.R. Troiano, Trans. AIME, 203, 413 (1955).
29. K. Löhberg and H. Westphal, Z. Metallk., 40, 449 (1958).
30. W. Knorr and H. Scholl, Z. Metallk., 51, 605 (1960).
31. M. Hansen and K. Anderko, "Constitution of Binary Alloys" McGraw-Hill, New York, 1959.
32. H. Giebelhausen, Z. anorg. Chem., 91, 25 (1915).
33. N. Schönberg, Acta Chem. Scand., 8, 624 (1954).
34. G.V. Samsonov and Ya.S. Umanskii, "Tverdye Soedineniya Tugoplavkikh Metallov" (Hard Compounds of Refractory Metals), Metallurgizdat, 1957.
35. M.A. Gurevich and B.F. Ormont, Dokl. Akad. Nauk SSSR, 96, 1165 (1954).
36. A. Osawa and M. Oya, Sci. Reports Tôhoku Univ., 19, 95 (1930).
37. E. Parthé, H. Nowotny, and H. Schmid, Monatsh., 86, 385 (1955).
38. R. Kieffer, F. Benesovsky, and H. Schmid, Z. Metallk., [B], 47, 247 (1956).
39. H. Nowotny, Monatsh., 85, 242 (1954).
40. R. Kieffer and F. Benesovsky, "Symposium on Powder Metallurgy", Iron Steel Inst., Special Rep. No. 58, 1954, p. 292.
41. Yu.M. Golutvin and T.M. Kozlovskaya, Zhur. Fiz. Khim., 34, 2350 (1960) [Russ. J. Phys. Chem., 1116 (1960)].
42. E.I. Gladyshevskii and Yu.B. Kuz'ma, Dopovidi Akad. Nauk Ukrain. SSR, 2, 1208 (1958).
43. H.J. Wallbaum, Naturwiss., 32, 76 (1944).
44. W. Köster and R. Haug, Z. Metallk., 48, 327 (1957).
45. S. Geller, B.T. Matthias, and R. Goldstein, J. Amer. Chem. Soc., 77, 1504 (1955).
46. H.A. Wilhelm, O.N. Carlson, and J.M. Dickinson, Trans. AIME, 200, 915 (1954); U.S. Atomic Energy Commission Publ. ISC-401 (1953).
47. S.T. Wlodek, J. Electrochem. Soc., 107, 923 (1960).
48. N.V. Eremenko, L.A. Tret'yachenko, and R.I. Yakhimovich, Zhur. Neorg. Khim., 5, 2290 (1960) [Russ. J. Inorg. Chem., 1110 (1960)].
49. B.A. Loomis and O.N. Carlson, in "Reactive Metals" (Edited by W.R. Clough), Interscience, New York, 1959, p. 227.
50. H. Hahn, Z. anorg. Chem., 258, 58 (1949).
51. G. Brauer (Editor), "Handbuch der Präparativen anorganischen Chemie" (Translated into Russian), Inostr. Lit., Moscow, 1956.
52. M. Zumbusch and W. Biltz, Z. anorg. Chem., 249, 1 (1942).
53. H. Nowotny, Monatsh, 82, 519 (1951).
54. H. Martsen and P. Duwez, Trans. Amer. Soc. Metals, 44, 484 (1952).
55. W.B. Pearson, J.W. Christian, and W. Hume-Rothery, Nature, 167, 110 (1951).
56. E.M. Savitskii, V.V. Baron, and Yu.V. Efimov, Trudy Inst. Metallurgii Akad. Nauk SSSR, No.IV, 230 (1960).
57. B. Childs, Phil. Mag., 5, 1267 (1960).
58. V.V. Baron, Yu.V. Efimov, and E.M. Savitskii, Izv. Akad. Nauk SSSR, Otd. Tekh. Nauk, 36 (1958).
59. R. Kieffer, Z. Metallk., 50, 18 (1959).
60. V.V. Baron, Yu.V. Efimov, and E.M. Savitskii, Izv. Akad. Nauk SSSR, Otd. Tekh. Nauk, Metallurgiya i Toplivo, 70 (1960).
61. H.A. Saller and F.A. Rough, Trans. AIME, 197, 545 (1953); U.S. Atomic Energy Commission Publ., AECD-2686 (1949).

62. S.T.Konobeevskii, "Sessiya AN SSSR po Mirnomy Ispol'zovaniyu Atomnoi Energii, Zasedanie OKhN" (Conference of the Academy of Sciences of the USSR on the Peaceful Uses of Atomic Energy, Meeting of the Section of Chemical Science), Izd.Akad.Nauk SSSR, Moscow, 1955.
63. W.B.Pearson, J.Iron Steel Inst., 164, 149 (1950).
64. A.Seybolt and H.Sumsion, Trans.AIME, 197, 292 (1953).
65. W.Rostoker and A.Yamamoto, Trans.Amer.Soc.Metals, 47, 1002 (1955).
66. A.J.Hren and C.M.Wayman, Trans.AIME, 218, 377 (1960).
67. W.Biltz and A.Köcher, Z.anorg.Chem., 241, 324 (1939).
68. B.Pedersen and F.Gronvold, Acta Cryst., 12, 995 (1959).
69. E.Hoschek and W.Klemm, Z.anorg.Chem., 242, 49 (1939).
70. P.Ehrlich, Z.anorg.Chem., 260, 1 (1949).
71. W.B.Pearson, J.W.Christian, and W.Hume-Rothery, Nature, 167, 20 (1951).
72. P.Greenfield and P.A.Beck, Trans.AIME, 200, 253 (1954).
73. P.Greenfield and P.A.Beck, Trans.AIME, 206, 265 (1956).
74. M.A.Tylkina, K.B.Povorova, and E.M.Savitskii, Dokl. Akad.Nauk SSSR, 131, 332 (1960).
75. R.Vogel and G.Tamman, Z.anorg.Chem., 58, 79 (1908).
76. F.Wever and W.Jellinghaus, Mitt.Kais.-Wilh.-Inst.Eisenforschg., 12, 377 (1930).
77. W.Köster and H.Schmid, Z.Metallk., 46, 195 (1955)
78. W.B.Pearson and W.Hume-Rothery, J.Inst.Metals, 80, 641 (1951-52).
79. W.Köster and W.Hache, Z.Metallk., 49, 647 (1958).
80. N.M.Matveeva, Candidate's Thesis, Institute of Metallurgy of the Academy of Sciences of the USSR, Moscow, 1955.
81. I.I.Kornilov and V.S.Mikheev, Dokl.Akad.Nauk SSSR, 104, 88 (1955).
82. M.I.Zakharova and P.N.Stetsenko, Vestnik Moskov.Gos. Univ., Ser.Khimii, No.5, 53 (1957).
83. M.I.Zakharova *et al.*, Dokl.Akad.Nauk SSSR, 119, 498 (1958).
84. P.Duwez, Trans.AIME, 191 (1951).
85. S.Saito, Acta Cryst., 12, 500 (1959).
86. W.Rostoker, J.Inst.Metals, 80, 698 (1951-52) (Discussion).
87. I.I.Kornilov, Zhur.Neorg.Khim., 3, 360 (1958).
88. I.I.Kornilov, "Nikel' i Ego Splavy" (Nickel and Its Alloys), Izd.Akad.Nauk SSSR, 1958.
89. I.I.Kornilov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1147 (1959).
90. J.H.Wenick, F.J.Morin, *et al.*, in "Proceedings of the International Conference on High Magnetic Fields, Massachusetts Institute of Technology, November 1961" 1–4.

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