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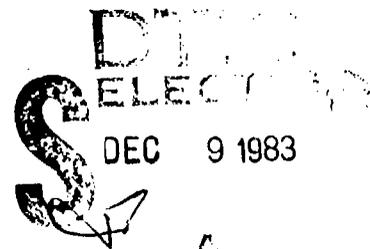
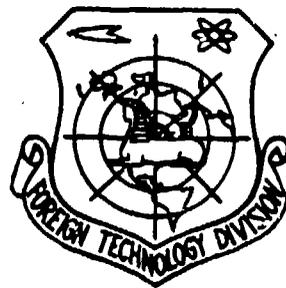
FOREIGN TECHNOLOGY DIVISION



CONSTITUTION DIAGRAM OF SYSTEM VANADIUM - COPPER

by

Ye.M. Savirskiy, V.V. Baron, et al



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By: Ye.M. Savitskiy, V.V. Baron, et al

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ë in Russian, transliterate as yë or ë.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh ⁻¹
cos	cos	ch	cosh	arc ch	cosh ⁻¹
tg	tan	th	tanh	arc th	tanh ⁻¹
ctg	cot	cth	coth	arc cth	coth ⁻¹
sec	sec	sch	sech	arc sch	sech ⁻¹
cosec	csc	csch	csch	arc csch	csch ⁻¹

Russian English

rot curl
lg log

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CONSTITUTION DIAGRAM OF SYSTEM VANADIUM - COPPER

Ye. M. Savitskiy, V. V. Baron, U. K. Duysemaliyev, Yu. V. Yefimov

Up to now, the constitution diagram of the system V - Cu has not been published. The data on the constitution diagram available in the literature are contradictory. L. Guillet [1] detected two compounds in alloys containing more than 29.4 at.% V, demixing in the region of 12.2-29.4 at.% V, and based on a microstructural analysis, he concluded that 7.4-8.6 at.% V is dissolved in copper in the solid state. On the other hand, in report [2] it is suggested that the solubility of vanadium in copper is very low. G. Norris [3] detected the eutectic at a content of \approx 8.6 at.% V. H. Gielbelhausen asserts that in the range of concentrations from 2.5 to 24.9 at.% V, the metals virtually do not mix in the liquid state. W. Rostoker and A. Yamamoto [5] made a microscopic study of alloys rich in vanadium (0.8-21.1 at.% Cu). According to their data, the boundaries of the solubility of copper in vanadium at 900° lie between 6.1 and 8.2 at.%. Interdendritic inclusions of copper were observed in the alloys with 8.2 and 21.1 at.% Cu. In reports [6, 7] it was established that the intermediate phases are absent in the system V - Cu, there is a wide region of demixing in the liquid and solid states, and limited solid solutions form on the basis of vanadium and copper.

The purpose of this study was to refine the preliminary results obtained in reports [6, 7] and to construct the complete constitution diagram of the system.

Table. Composition of V - Cu alloys and thermal analysis data.

(1) Состав сплавов						(2) Данные термического анализа		
по шихте, (3) вес. %		по химическому (4) анализу, вес. %		по ат. % (5)		(6) Температура плавления мед- ной фазы (ниж- ний солидус), °C	(7) Температура солидус, °C	(8) Темпера- тура лик- видус, °C
V	Cu	V	Cu	V	Cu			
100	—	—	—	100	—	—	1890	—
99.7	0.3	—	0.26	99.8	0.2	—	—	—
99.5	0.5	—	0.45	99.64	0.36	—	1885	—
98.0	2.0	—	1.51	98.79	1.21	—	1800	1885
95.0	5.0	—	5.07	95.9	4.1	—	1635	1850
93.0	7.0	—	—	94.3	5.7	—	1590	—
92.5	7.5	—	7.41	94.0	6.0	—	1585	1805
92.0	8.0	—	—	93.5	6.5	—	1575	—
91.0	9.0	—	—	92.7	7.3	—	1550	1780
90.5	9.5	—	9.68	92.1	7.9	—	1535	—
90.0	10.0	—	—	91.8	8.2	1130	1530	1750
84.0	16.0	—	—	86.8	13.2	1122	1530	1555
83.5	16.5	—	—	86.35	13.65	—	1530	1120
83.0	17.0	—	—	85.9	14.1	—	1535	1100
75.0	25.0	—	—	78.9	21.1	1120	1830	—
50.0	50.0	—	—	55.5	44.5	1120	1830	—
11.0	89.0	10.59	—	12.9	87.1	1120	—	—
8.0	92.0	7.97	—	9.8	90.2	1118	—	—
7.0	93.0	6.76	—	8.3	91.7	1120	—	—
3.5	96.5	3.29	—	4.0	96.0	1120	—	—
2.5	97.5	2.25	—	2.8	97.2	1122	—	—
1.0	99.0	0.64	—	0.8	99.2	1120	—	—
0.5	99.5	0.34	—	0.42	99.58	1108	—	—
0.1	99.9	0.07	—	0.09	99.91	1092	—	—
—	100	—	—	—	100	1083	—	—

KEY: (1) Composition of alloys. (2) By charge, wt. %. (3) By chemical analysis, wt. %. (4) By at. %. (5) Thermal analysis data. (6) Melting point of copper phase (solidus index, °C). (7) Solidus temperature, °C. (8) Liquidus temperature, °C.

Preparation of Alloys. The original materials were carbothermal vanadium (99.7 %) and electrolytic copper brand MO. The vanadium contained 0.17 wt. % C, 0.02 wt. % N and 0.1 wt. % O; the maximum content of all the admixtures in the copper did not exceed 0.05 wt. %. The alloys rich in vanadium and weighing 10-20 g were melted in an electric arc furnace with a permanent tungsten electrode in a helium atmosphere at a pressure of 0.5 atm. The alloys based on copper, weighing 300 g, were melted in corundum crucibles in a high-frequency furnace in an argon atmosphere (0.7 atm.). In order to obtain uniformity of composition throughout the ingot, each alloy was remelted several times. The results of the chemical analysis and the composition of the alloys obtained are given in the table. The cast alloys were subjected to homogenization annealing in evacuated quartz ampoules at 900° for 50-100 hours. The copper-based alloys were preliminarily hot hammered with 50% reduction. The vanadium-rich alloys were

cold hammered (degree of deformation of 5-10%).

Study Procedure. In order to study the phase equilibriums in the system, the methods of microscopic, thermal and X-ray analyses were used. Furthermore, the microhardness was measured, and some other properties of the vanadium- and copper-based alloys were studied.

The microstructure of the alloys was studied in the cast, annealed and hardened states. The homogenized alloys containing up to 13 at.% Cu were hardened in water at 900, 1200 and 1500° after holding 100, 50 and 1 hours, respectively, while the copper-based alloys (up to 12.9 at.% V) - at 500 and 950° after holding for 4 hours. Heat treatment of the alloys at 1500° was carried out on a special device for high-temperature hardening, and at lower temperatures - in evacuated quartz ampoules. The sections of the vanadium-rich alloys were etched by a mixture of hydrofluoric (95%) and nitric (5%) acids, and the copper-vanadium alloys - by concentrated nitric acid.

The X-ray pictures were taken with powders in camera RKU on K_{α} - Cu emission, and with the section, in camera type Kros-1 on K_{α} - Co emission.

The melting point of the alloys (liquidus, solidus) was determined by two methods: drop and differential microthermal, the procedure for which was described in detail in earlier reports [6-8]. Both methods gave good agreement of the results.

The microhardness H_{μ} was measured on instrument PMT-3 with a load of 20 and 100 g. The hardness of the vanadium-rich alloys was determined according to Vickers with a load of 5 kg, and the copper-based alloys - according to Brinell with a load of 250 kg, a sphere diameter of 5 mm, and holding for 30 seconds. The electrical resistance was measured by the compensation method on annealed wires with ϕ 0.5 mm.

Results of Study. The macro- and microscopic analysis revealed demixing of the cast alloys containing from 13.65 to 96.0 at.% Cu

into two layers: α - a vanadium-rich layer, and β - a copper-rich layer. Demixing was not observed in the alloys containing less than 13.65 at.% Cu. In the alloy with 13.65 at.% Cu, a very thin layer of the copper phase was observed in the lower part of the ingot. As the copper content in the alloys increased, the thickness of the β -layer increases, already becoming very large in the alloy with 21.1 at.% Cu (Fig. 1). Inclusions of the copper phase which are irregularly distributed primarily on the grain boundaries of the vanadium phase are visible in the α -layer of the alloys, and in the β -layer,

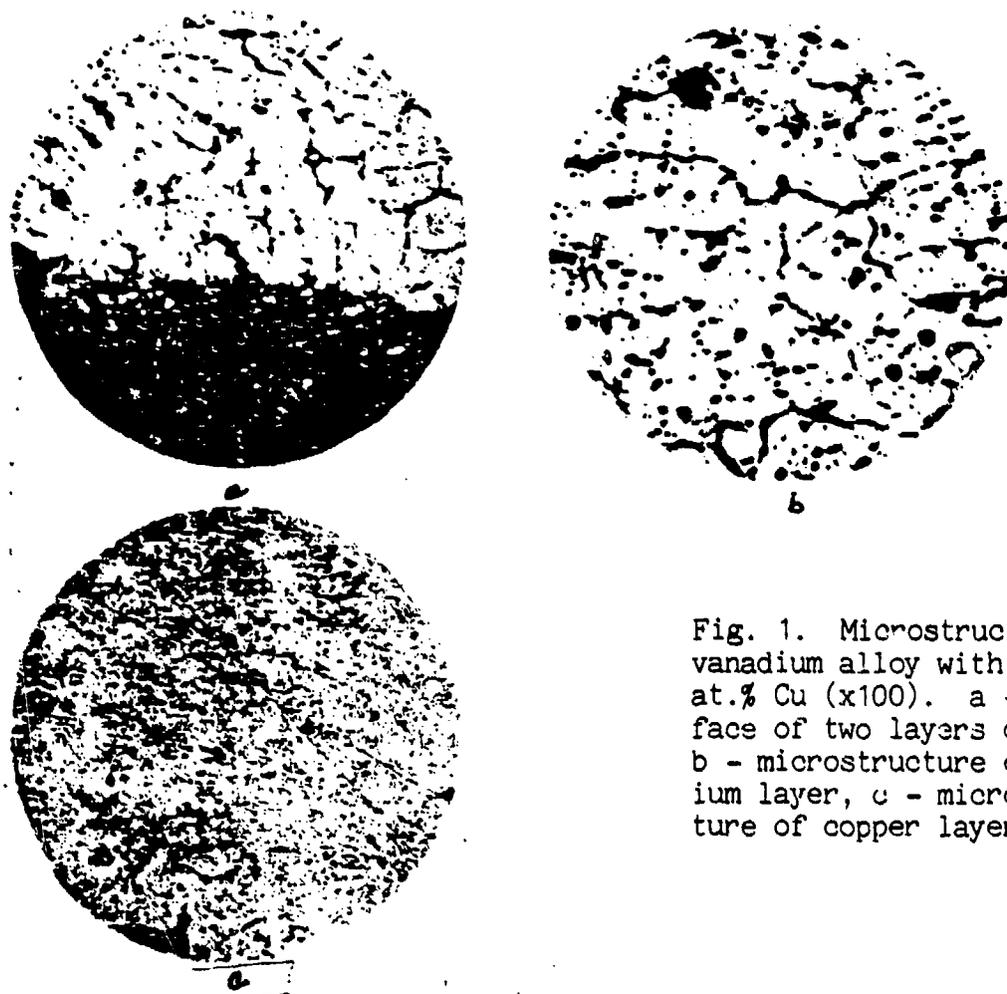


Fig. 1. Microstructure of vanadium alloy with 21.1 at.% Cu (x100). a - interface of two layers of alloy; b - microstructure of vanadium layer, c - microstructure of copper layer.

bluish oval embedments which are rich in vanadium, and the position of which is not connected with the structure of the matrix.

Demixing was not detected, either, when studying the macro- and microstructure of copper-based alloys containing less than 4.0 at.% V. In the cast state, these alloys and the alloys containing 6.5-13.2 at.% Cu were two-phase. After annealing, the one-phase state was established in the alloys containing up to 6.0 at.% Cu (Fig. 2a).

Finely-dispersed inclusions of the second phase appeared in the alloy with 6 at.% Cu (Fig. 2b). With the further increase in the copper contents in the alloys (up to 13.2 at.%), the quantity of the copper phase on the grain boundaries increases (Fig. 2c, d). Homogenization annealing did not change the structure of the copper-based alloys, except for the alloy with 0.09 at.% V, which became one-phase (Fig. ce). As the vanadium content in the copper increases (up to 4 at.%), the quantity of the second phase increases (Fig. 2f-h). No signs of the eutectic were detected in the copper-based alloys. Thus, around 6 at.% Cu dissolves in vanadium at room temperature, and in copper - around 0.1 at.% V. As the temperature increases, the solubility of copper in vanadium in the solid state increases; after hardening, the solid solution was recorded in the alloys containing up to 6.5 at.% Cu at 900°, up to 7.3 at.% Cu - at 1200°, and up to 7.9 at.% Cu - at 1500°. In the copper-rich alloys, only the alloy with 0.09 at.% V

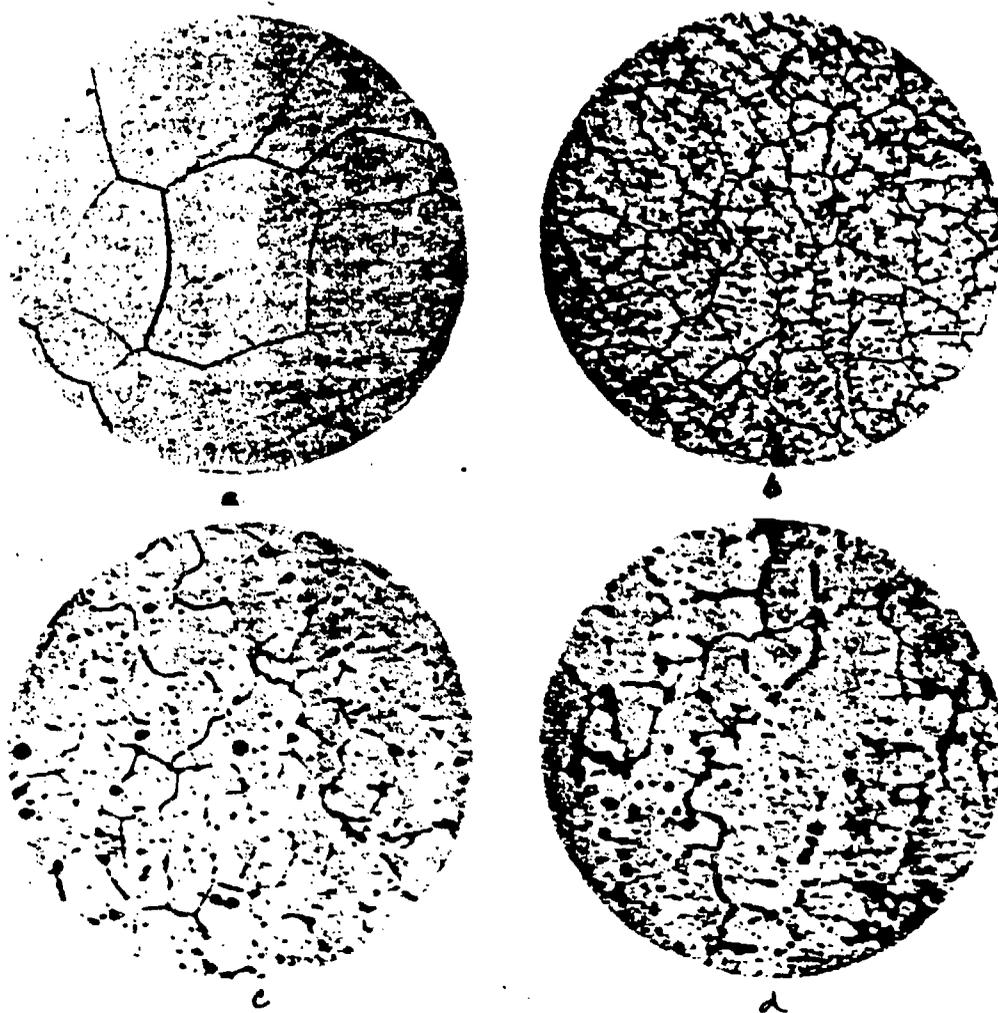


Fig. 2.

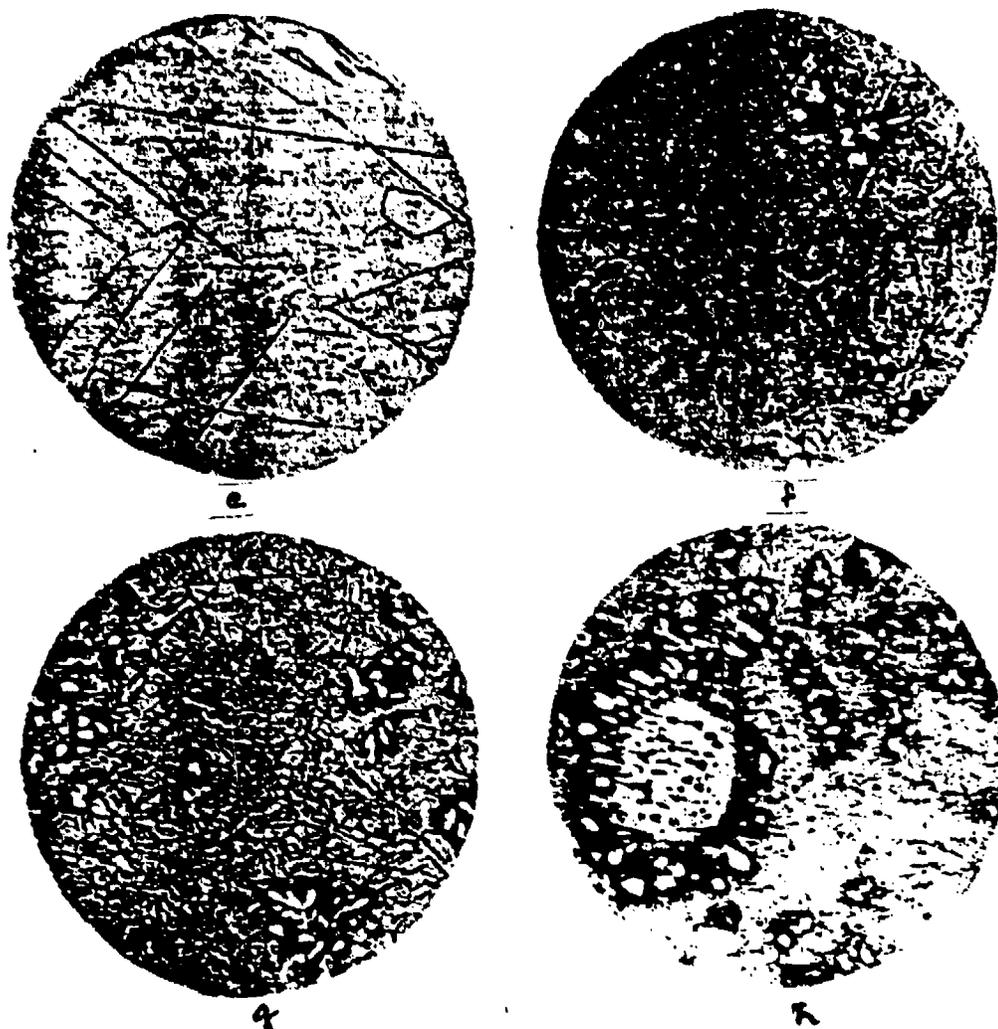


Fig. 2 (cont'd from preceding page). Microstructure of annealed alloys of vanadium-copper system: a - V + 5.7 at.% Cu (x100); b - V + 6.0 at.% Cu (x100); c - V + 6.5 at.% Cu (x100); d - V + 13.2 at.% Cu (x100); e - Cu + 0.09 at.% V (x300); f - Cu + 0.8 at.% V (x300); g - Cu + 2.8 at.% V; h - Cu + 4.0 at.% V (x300).

was one-phase at 500 and 950°. However, the slight decrease in the quantity of the second phase in the two-phase alloys after hardening at 500 and 950° indicates the increase in the solubility of vanadium in copper with the increased temperature.

The X-ray structural analysis established the presence of only two phases in the alloys: the α - solid solution, rich in vanadium with a body-centered cubic lattice, and the β - solid solution, rich in copper with a face-centered cubic lattice. The lattice constants were not precisely measured because of the blurriness of the X-ray diffraction lines. Qualitatively, an increase in the constants of the copper and vanadium lattices was observed during the dissolution of the second component.

According to the data of the thermal analysis (see the table), the addition of copper to vanadium lowers its melting point from 1890° to the temperature of the monotectic equilibrium, which is equal to 1530° . The point of inflection on the solidus curve corresponds to the maximum solubility of copper in vanadium in the solid state (around 8 at.% at 1530°). The liquidus temperature also decreases with the increase in the copper content, reaching the monotectic equilibrium temperature at 13-14 at.% Cu. An interruption at 1120° corresponding to the melting point of the copper phase was recorded on the thermograms of the alloys containing from 8 to 99.6 at.% Cu. Alloying copper with vanadium (up to 0.8 at.%) increases the initial melting point of the alloys (from 1083 to 1120°). The alloy with 0.09 at.% V melts in the range $1092-1100^{\circ}$. The point of intersection of the solidus curve with the peritectic horizontal corresponds to the maximum solubility of vanadium in copper in the solid state (0.8 at.% at 1120°).

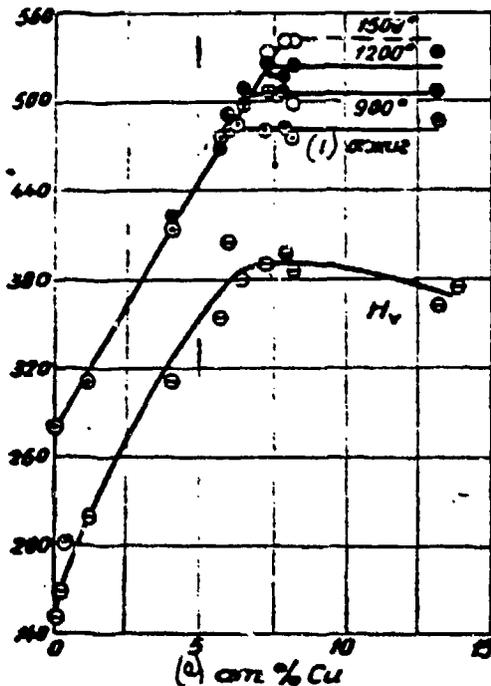


Fig. 3. Hardness and microhardness of solid solution based on vanadium in annealed (H_V - \odot , H_H - \ominus) and hardened (at 900° - \bullet , at 1200° - \bullet , at 1500° - \circ) states. KEY: (1) Annealing. (2) at.% Cu.

Increasing the copper content in vanadium (within the limits of the solid solution) causes an increase in the hardness and microhardness of the alloys (Fig. 3). In the two-phase range, the hardness remains constant in a certain range of concentrations, and then begins to decrease with the increase in the quantity of the softer second phase. The results of the microhardness measurements on the hardened alloys (Fig. 3) completely confirm the data of the microstructural analysis about the increase in the solubility of copper in

vanadium with an increase in temperature. Alloying vanadium with copper leads to a decrease in its plasticity. During cold upsetting,

the first cracks appeared in pure vanadium at 71% deformation, and in the alloy with 1.2 at.% Cu - already at 26.5% deformation.

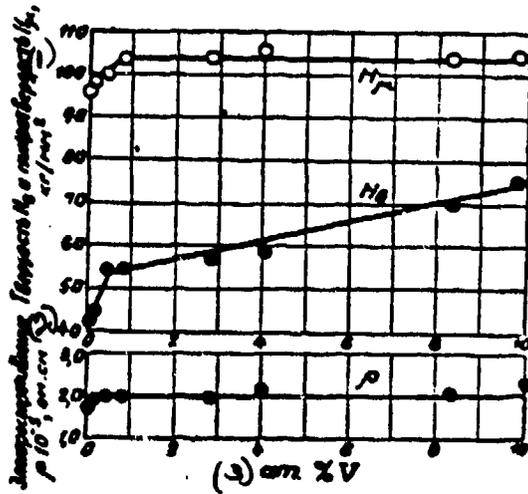
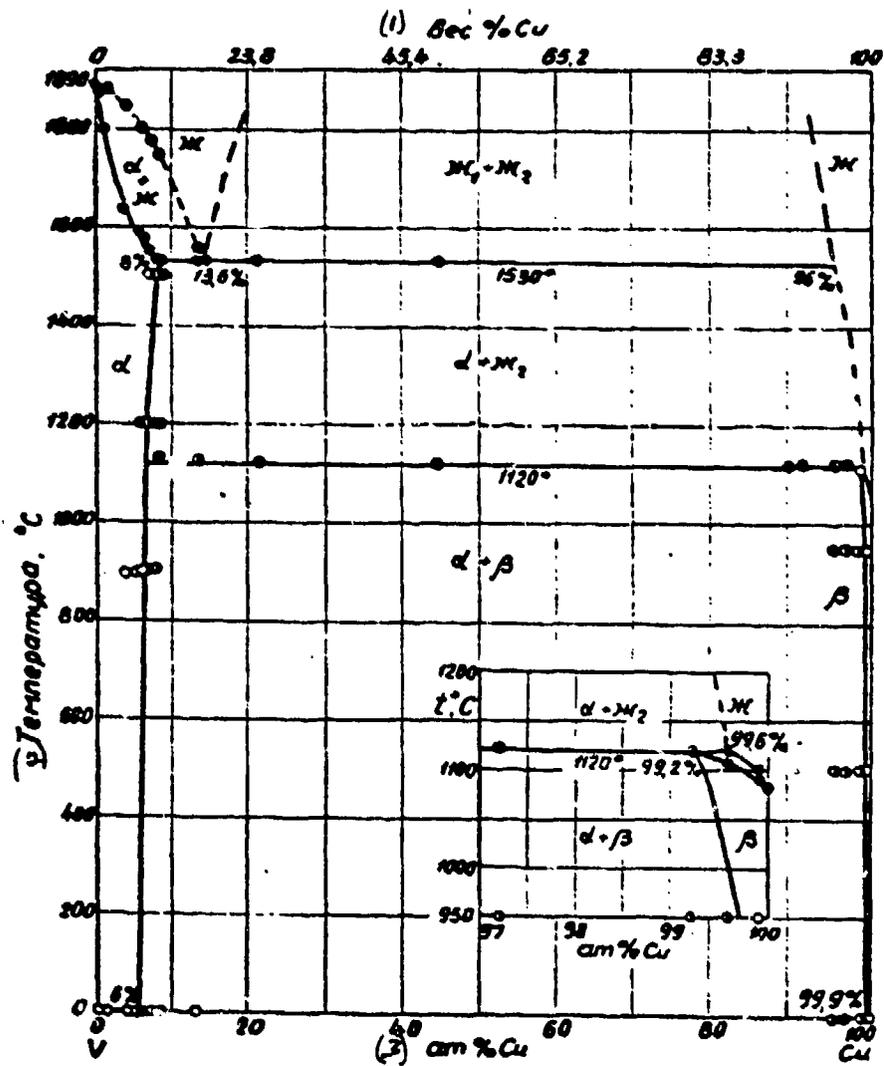


Fig. 4. Properties of alloys based on copper.

KEY: (1) Hardness H_B and microhardness H_U , kg/mm^2 . (2) Electrical resistance ρ , 10^{-5} , ohms.cm. (3) at.% V.

Fig. 5. Constitution diagram of system vanadium - copper.
KEY: (1) Wt. % Cu.
(2) Temperature.
(3) at.% Cu.



The increase in the hardness, microhardness and electrical resistance of the copper-based alloys with the increase in the vanadium content (Fig. 4) also confirms the formation of the solid solution of vanadium in copper.

Figure 5 shows the constitution diagram of the vanadium - copper system constructed from all of the experimental data.

Conclusions

The constitution diagram of the system vanadium - copper was constructed from the data of the microstructural, thermal and X-ray analysis and studies of the hardness, microhardness and electrical resistance of certain alloys.

A wide range of immiscibility in the liquid and solid states which extends from 13.6 to 96.0 at.% Cu at a temperature of 1530° was detected in the system. Vanadium and copper form limited solid solutions. The solubility of copper in vanadium at room temperature is around 6 at.%. As the temperature increases, the solubility of copper in vanadium increases, reaching a maximum of approximately 8 at.% at 1530°. The solid solution based on copper is formed by the peritectic reaction $\gamma + \alpha \rightarrow \beta$ at 1120°. The maximum solubility of vanadium in copper at the peritectic temperature is 0.8 at.%, and at room temperature - on the order of 0.1 at.%. Intermetallic compounds are not formed in the system.

Copper dissolved in vanadium increases its hardness and markedly decreases plasticity. The addition of small amounts of vanadium increases the hardness and electrical resistance of copper.

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