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PHASE DIAGRAM OF THE V-La SYSTEM

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PHASE DIAGRAM OF THE V-La SYSTEM

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Pure metallic vanadium has become more available for in-
vestigation only quite recently, so that the structure of
its alloys has not been sufficiently studied. There is an
absolute lack of data on the physicomechanical properties and
the phase diagrams of vanadium with the rare-earth metals.

The present work was undertaken with the purpose of con-
structing a phase diagram of the V-La alloys. For this, use
was made of microstructural, thermal and, for certain alloys,
radiographic analyses; and the hardness, micro-hardness and
plasticity under compression of 23 alloys of vanadium with
lanthanum were measured.

The basic materials used were carbothermal vanadium
(99.3% V) and 98.5% pure lanthanum. The vanadium contained
the following basic admixtures: 0.25% C, 0.02% N, 0.228% P
and not more than 0.2% metallic admixtures; lanthanum 0.04;
Fe, heavy metals (Pb, Cd, Bi, Sn) less than $3 \cdot 10^{-4}\%$;
remainder, the sum of rare-earth elements, chiefly cerium.

The alloys were melted in an arc furnace with a non-con-
sumable tungsten electrode on a water-cooled copper bottom
in a helium atmosphere (0.5 at) after evacuation to 10^{-3} mm
of mercury and flushing of the furnace with helium. Before
melting each alloy, a getter of titanium iodide was melted
up for additional purification of the inert gas. The charge
of 50 g consisted of small pieces of vanadium and lanthanum.

The latter, before being weighed, was carefully cleaned with ether of the oil in which it was kept to protect it from oxidation, and stripped of the surface oxide film on an energy stone. To secure uniform composition throughout the ingot, each alloy was subjected to a quadruple remelting. The quality of the melts was checked by measuring the hardness of the control sample of titanium iodide. This method is very sensitive, since the hardness of titanium depends - -very greatly upon the oxygen and nitrogen content in it (1).

To obtain alloys with low lanthanum content (less than 0.5%), a binder (2.5% La) was first prepared, which after chemical analysis was then introduced into the pure vanadium.

The chemical analysis of the alloys obtained is shown in Table 1. Some alloys (up to 4% La) after quadruple melting were poured in the arc furnace into molds for small rods of square cross-section (10 x 10 mm.) by means of a special hearth.

The alloys containing more than 0.4% La oxidized very strongly in air. Hence, the samples were kept in vacuum oil. The alloys with a smaller lanthanum content did not oxidize at room temperature.

Table 1

Composition of Alloys of Vanadium with Lanthanum and Thermal-Analysis Data

Состав сплавов, %			Темпера-тура со-лидуса, °C	Темпера-тура лик-видуса, °C	Темпера-тура обра-зования β-твердого раствора, °C	Темпера-тура обра-зования α-твердого раствора, °C
по шихте		по хими-ческому анализу, La				
V	La					
100	—	—	1880			
99,9	0,1	0,07	1844			
99,8	0,2	0,14	1785			
99,7	0,3	0,23	1752	1880		
99,6	0,4	0,37	1710			
99,5	0,5	0,47	1680			
99,3	0,7	0,77	1684	1870		
99,0	1,0	0,89	1678	1870		
98,5	1,5	1,3	1680	1808	900	710
97,0	3,0	2,54	1688	1808	898	
96,0	4,0	3,89	1680	1730	895	
95,0	5,0	—			887	
93,5	6,5		1672*		890	
85	15		1680*		890	
80	20				890	
70	30		1684*		887	700
65	35				885	700
50	50					707
40	60					700
10	90					700
5	95					700
0,5	99,5					685—700
—	100					675

Legend: (1) Composition of alloys % (2) By charge (3) By Chemical Analysis

(4) Solidus temperature (5) Liquidus Temperature (6) Temperature of formation of β-solid solution

(7) Temperature of formation of α-solid solution

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INVESTIGATION OF MACROSTRUCTURE AND MICROSTRUCTURE OF ALLOYS

Macroscopic and microscopic analyses revealed lamination of the cast alloys containing from 5 to 95% lanthanum into two sharply separated layers: a γ-lamina, rich in vanadium, and an α-lamina, rich in lanthanum. The γ-lamina contains considerable quantities of the softer second phase, lying mainly along the boundaries of the polyhedral grains. In the α-lamina, drop-shaped light-colored inclusions, rich in vanadium and not connected with the basic structure, are sometimes observed (Fig. 1).
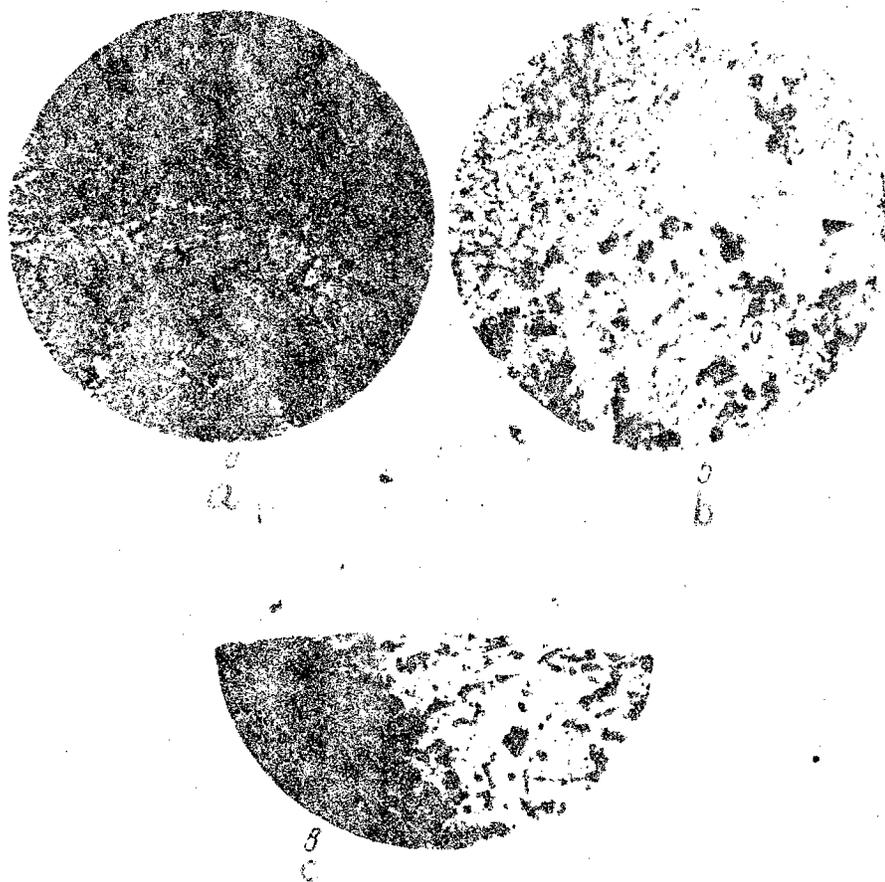

Fig. 1. Microstructure of Alloy (x100) of Vanadium with Lanthanum (50% V, 50% La) from Area of Lamination (Roasted State, Etching HF + 5% HNO_3):
Legend: A. of γ-lamina; B. of α-lamina;
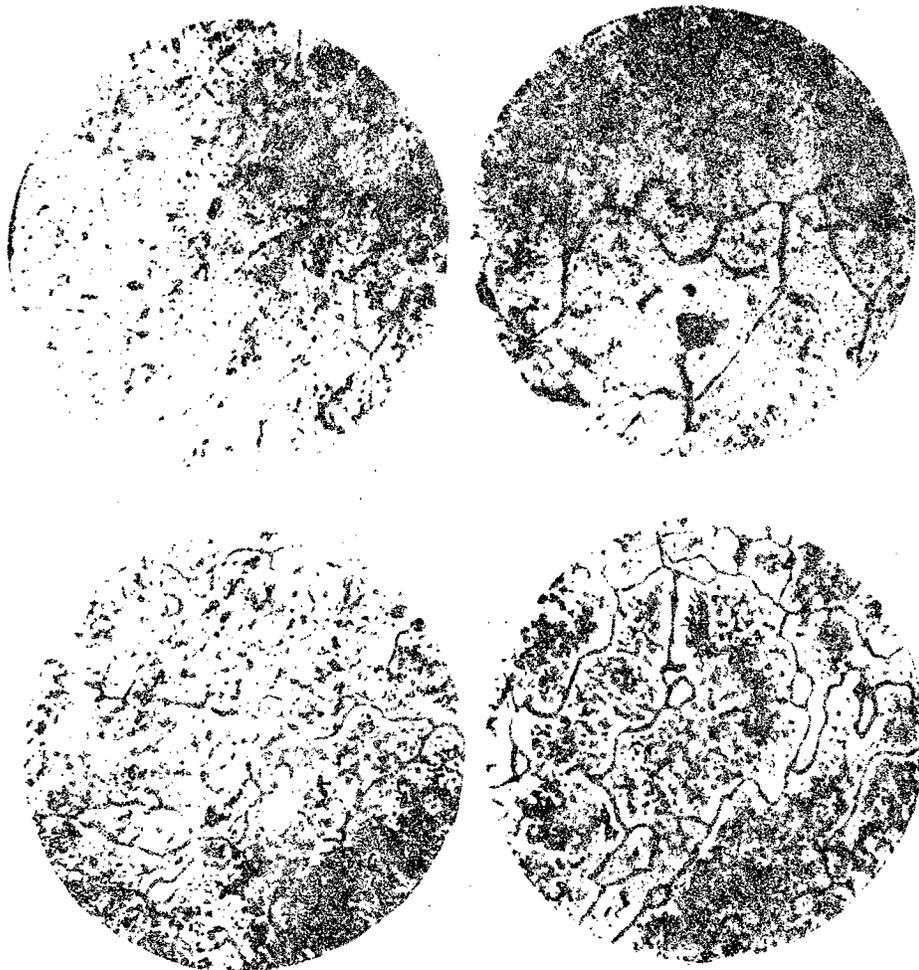C. Boundary between two laminas of alloy.

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Figure 2. Microstructure of Alloys (X 100) Rich in Vanadium, in Roasted State (Etching HF + HNO₃)

Legend: a) 100% V; b) 0.07% La; c) 0.14% La; d) 0.23% La
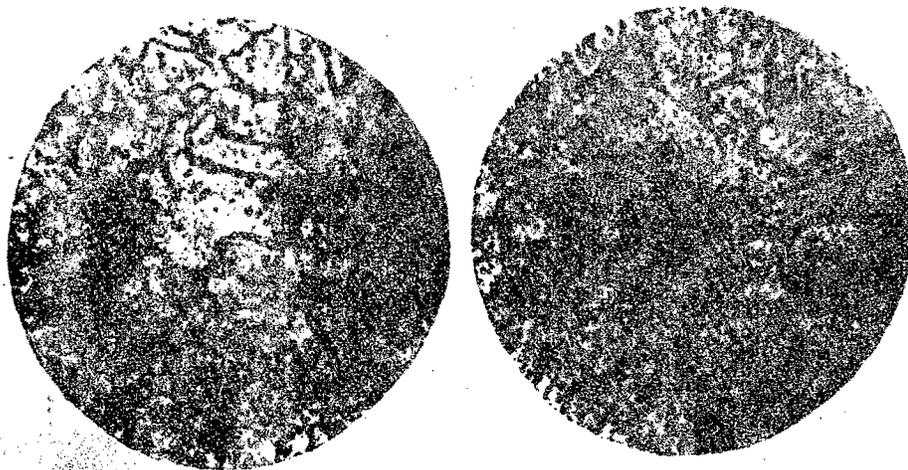
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Figure 2. Continued: e) 1.3% La; and f) 3.89% La.

In the alloys containing less than 4% La, no lamination is observed. These alloys are two-phased in the cast state. No traces of lamination were detected either in examining the macrostructure and microstructure of the alloy with 99.5% La.

Homogenizing roasting of all the alloys in evacuated quartz ampules for 100 hours at 800° did not change the structure of the alloys, except for the alloy with 0.07% La, which became one-phase (Fig. 2,b).

Thus, in the vanadium-lanthanum phase diagram there is a wide area of non-miscibility in the liquid and solid states. The boundary of this area on the vanadium side lies between 4 and 5% La, and on the lanthanum side between 95 and 99.5% La. The presence of a clear dividing line between these two layers after roasting indicates the absence of intermediate phases between them (see Fig. 1). The roasting of the cast two-phase alloys rich in vanadium resulted in the coagulation of the small inclusions of the second phase along the boundaries of the grains of the solid vanadium solution (Fig. 2, c-f).

From a comparison between the microstructure of the alloy with 0.07% La and those of vanadium and the alloys with a larger lanthanum content it may be assumed that the solu-
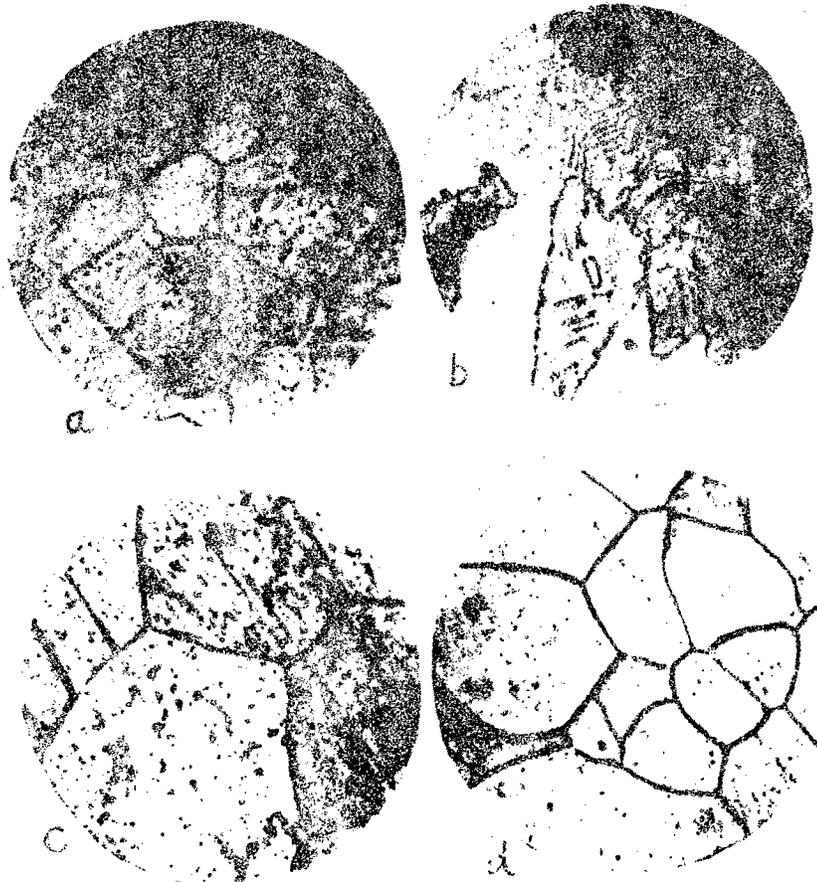
Figure 3: Microstructure of Alloys (X 100) Rich in Vanadium, in Annealed State (Etching HF + 5% HNO3; Annealing Temperature Indicated in Parentheses).

Legend: a) 0.7% La (1100°); b) 0.14% La (1100°);
c) 0.14% La (1500°); d) 0.23% La (1500°);
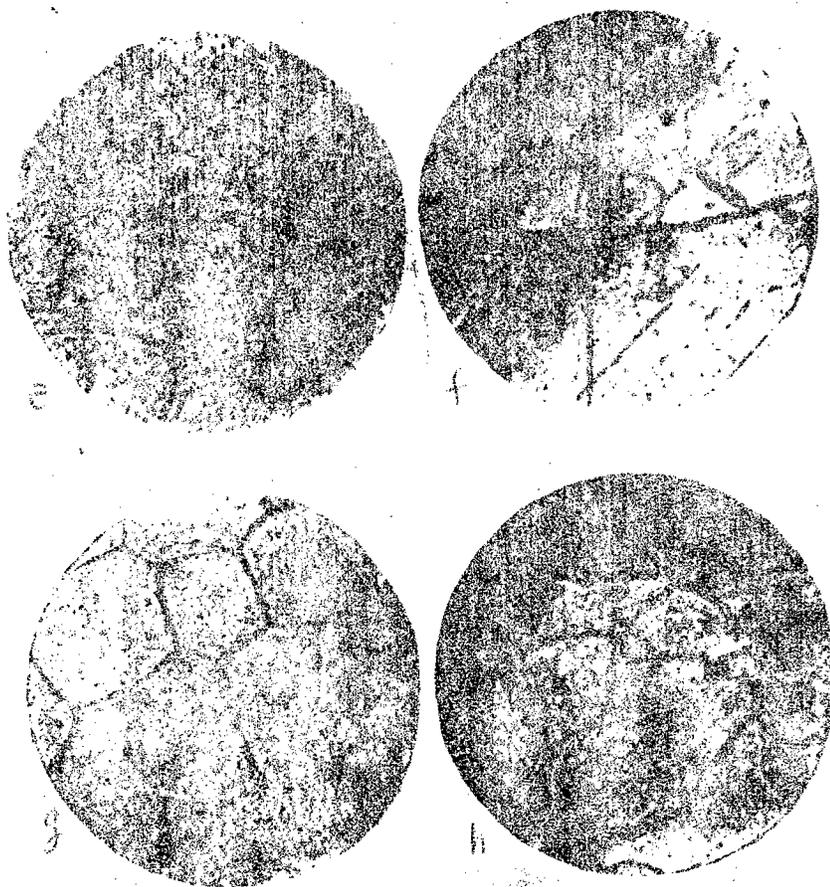
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Figure 3. Continued: e) 0.37% La (1500°); f) 0.14% La (1650°); g) 0.37% La (1650°); and h) 0.47% La (1650°).

bility of lanthanum is vanadium at room temperature is about 0.1% La. Roasting the alloys rich in vanadium at 1100° for 100 hours results in a certain growth in the grain and further coagulation of the second phase.

The investigation of the micorstructure of the alloys rich in lanthanum required special methods of preparing slides, which were polished on a cloth moistened with alcohol and were photographed immediately after preparation and etching (1-2 minutes). However, this did not always produce good-quality photos. Examination of the microstructure of alloys rich in lanthanum did not give positive results owing

to the presence in the lanthanum of admixtures forming eutectic with it. The structure of these alloys can only be judged from the data on the thermal analysis and their properties.

To determine the limit of solubility of lanthanum in vanadium in the solid state phase microstructural analysis was employed. The roasted alloys with a lanthanum content up to 1% were kept in a vacuum and heated by passing a current through them at 1100, 1500 and 1650° for 10 hours, 1 hour and 30 minutes, respectively, and were annealed from these temperatures in water on a special installation for determining the melting point and annealing refractory alloys. The solid solution was fixed in alloys containing up to 0.14% La at 1100°, up to 0.37% La at 1500°, up to 0.47% La at 1650° (Fig. 3).

At these temperatures the alloys with larger lanthanum content were two-phased. The microstructural phase analysis data indicate an increase in the solubility of lanthanum in vanadium with increase in temperature.

THERMAL ANALYSIS

The melting point of the refractory alloys rich in vanadium was determined by the drop method with the aid of an optical pyrometer in a vacuum on the above-mentioned installation. The samples were heated by passing a current through them from an OSU-40 transformer. The pyrometer was graduated under like-type conditions by melting points of the pure metals (nickel, titanium and zirconium). The incipient fusion point was fixed by the appearance of a drop in the depression of the sample D/h ~ 1/4), the end temperature of fusion at the moment of the breaking of contact in the melting of the samples at the place of weakened section. The thermal analysis data are given in Table 1.

The introduction of up to 0.4% lanthanum into the vanadium results in a sharp lowering of the incipient fusion point of alloys (from 1880 to 1680°). Further increase in the lanthanum content does not change this. The bend in the solidus curve corresponds to the maximum solubility of lanthanum in vanadium at 1680°. The liquidus line also drops with increase in lanthanum content, and at a content of 4 to 5% La the melting point is 1680°, which corresponds to their monotectic equilibrium.

The thermal analysis of the alloys rich in lanthanum was

done on a Kurnakov pyrometer with the use of a standard platinum-platinorhodium thermocouple in evacuated quartz ampules (see Table 1). The alloys were cut up into small pieces and put into the quartz ampules, from which the air was pumped out. Then they were heated to 1100°, whereupon only the α-lamina melted in the alloys containing from 30 to 95% La, while the refractory δ-lamina (1680°) remained in the solid state. The conversions undergone by the α-lamina were recorded while cooling at a rate of 5° a minute. Two bends are observed on each of the cooling curves obtained, which were recorded not less than two times for each alloy. The first bend on the cooling curve for pure lanthanum, at 885°, corresponds to its melting point. For all the alloys, the first bend is observed at 890°, which apparently corresponds to the formation of a solid lanthanum solution by anatectic reaction. The second bend, observed on the cooling curve of lanthanum of the given degree of purity at 675°, corresponds to its polymorphous conversion, which coincides with the data in the literature (1). In alloys containing from 30 to 95% La, the second bend is detected at 700°; in alloys with 0.5% V the beginning of the bend of the curve is at 685°, the end at 700°. These temperatures correspond to the conversion in the solid state of the cubic face-centered lattice of the β-solid lanthanum solution into the hexagonal lattice of the α-solid solution by anatectic reaction: $\delta + \beta \rightleftarrows \alpha$. Thus, the vanadium raises the temperature of the polymorphous conversion of the lanthanum by 25°, and the melting point by 5°. The low-temperature conversion of lanthanum (about 300°), which takes place according to the literature data (2, 3), was not detected by us.

MECHANICAL PROPERTIES

Figure 4 shows the data on hardness and plasticity of roasted alloys under compression. Small additions of lanthanum produce an increase in the hardness of alloys owing to the formation of a solid solution and then a dispersion secretion of the second phase. Here the plasticity, remaining constant in the limits of the solid solution (0.1% La), diminishes sharply with the appearance of the second phase in the alloys, clearly confirming the limit of solubility of lanthanum in vanadium detected by microstructural phase analysis. With a further increase in the lanthanum content, the hardness gradually diminishes, and the plasticity increases, which is apparently to be explained by the increase in the quantity of the softer second phase.

Upon passage into the area of lamination (4-5% La) the hardness of the lamina of the γ-solid solution continues to diminish evenly to a certain limit (200 kg/sq mm), which, beginning with 20% La, does not change with an increase in the lanthanum content. The hardness of the lamina of the α-solid solution drops from 54 kg/sq mm for an alloy with 20% La to 40 kg/sq mm, which remains unchanged up to 99.5% La. The hardness of the α-solid solution of the alloys is somewhat greater than that of pure lanthanum (37.4 kg/sq mm), which confirms the presence of a certain solubility of vanadium in lanthanum.
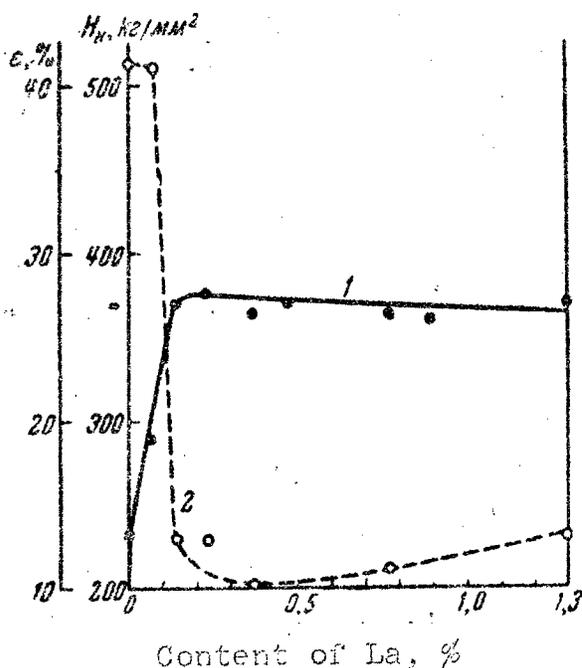

Fig. 4. Properties of alloys of vanadium with lanthanum in the roasted state:
1. Hardness H_K ; 2. plasticity under compression φ_{CT}

X-RAY STRUCTURAL ANALYSIS

The X-raying of alloys containing 0.23 and 1.3% La was done from powders in an RKD chamber on copper radiation with filter. The computation of the radiographs confirmed the presence in the alloys of two solid solutions: a γ-solution, rich in vanadium, with a volume-centered cubic lattice, and an α-solution, rich in lanthanum, with a hexagonal

lattice. Because of the blurring of the radiograph lines, no precise measurement of the parameters of the lattice was made. The tentative value of the lattice parameter of the saturated γ-solid solution is a = 3.037 Å. The vanadium lattice parameter (X-raying was done under the same conditions) is a = 3.032 Å. Thus, the introduction of lanthanum into the solid solution results in a certain increase of the vanadium lattice parameter.

A comparison between the radiographs of lanathanum and the alloys also confirms the presence in the alloys of a lanthanum-base solid solution. Dissolving vanadium in lanthanum results in a certain distortion of the lanathanum lattice (c/a = 6.016 for lanthanum, 6.020 for the alloys).

The phase diagram of the alloys of the vanadium-lanthanum system constructed by us from the entirety of the experimental data is given in Figure 5.
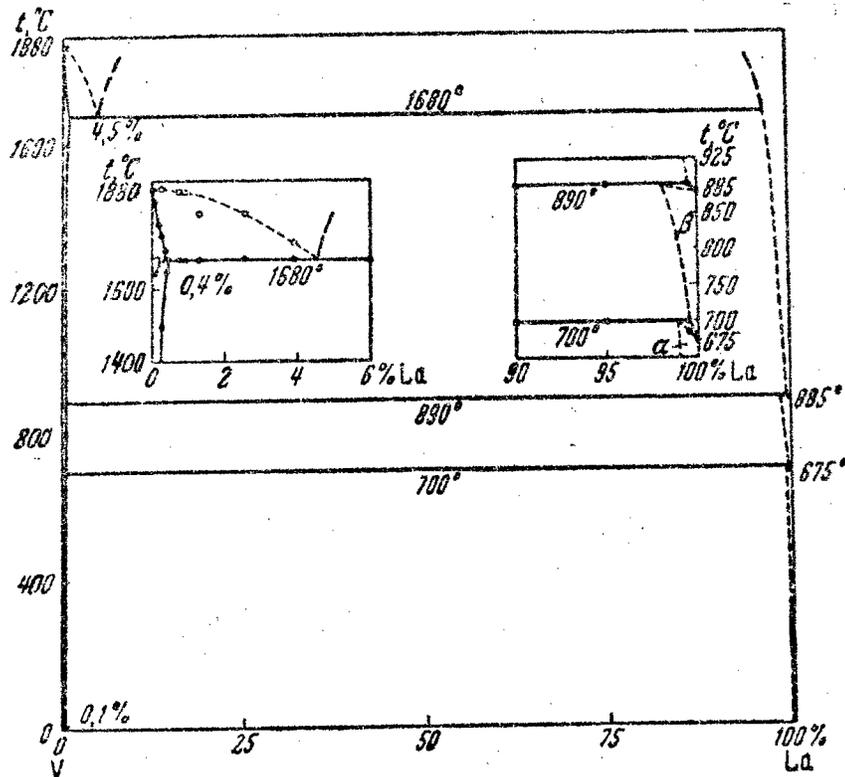

Fig. 5. Phase diagram of the Vanadium-Lanthanum Alloys.

CONCLUSIONS

1. A phase diagram of V-La has been constructed.

2. A wide area of lamination in the liquid and solid states is observed in the vanadium-lanthanum system, extending at a monotectic temperature of 1680° from 4-5% to 95-99.5% lanthanum.

3. Lanthanum and vanadium form areas of limited solid solutions. The limit of solubility of lanthanum in vanadium at 20° is about 0.1%. With increasing temperature, the solubility of lanthanum in vanadium grows, reaching a maximum (0.4%) at 1680°. The solubility of vanadium in α- and β-lanthanum is less than 0.5% V and also increases with rising temperature.

4. A lanthanum-base β-solid solution is formed by anatectic reaction $zh + \gamma \rightleftarrows \beta$ at 890°; the α-solid solution by anatectic reaction $\gamma + \beta \rightleftarrows \alpha$ at 700°.

5. Small additions of lanthanum considerably increase the hardness of vanadium, without lowering its plasticity in the limits of the solid solution.

6. Alloys of vanadium with lanthanum containing over 0.4-0.5% lanthanum by weight are not stable in air.

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