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STRUCTURE DIAGRAM AND SOME PROPERTIES OF ALLOYS OF THE SYSTEM NIOBIUM- [redacted] MOLYBDENUM -[redacted] VANADIUM

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The purpose of the present paper is the determination of the structure diagram and investigation of certain properties of alloys of the system Nb-Mo-V.

The structure of the binary systems Nb-Mo, Nb-V and Mo-V has been investigated by means of metallographic and x-ray analyses (1-3). In all these systems we observe an unlimited interfusibility of the components in the liquid and solid states. The study of the properties of individual alloys of these systems yielded better results with regard to strength and high-temperature corrosion resistance than the original method (4-8). There are hardly [any] data on the properties of alloys of the system Nb-Mo-V. The ternary structure diagram of the alloys of this system has also not been plotted as yet. Owing to the presence in the binary system Nb-Mo, Nb-V, Mo-V of a continuous series of solid solutions, and in view of the closeness of atomic radii and the identity of their crystalline structures, it could be assumed that there is an unlimited solubility also in the ternary system Nb-Mo-V.

Nevertheless, the determination of this structure diagram and the study of the properties of these alloys is of the greatest interest since they may constitute the basis of a heat-resisting and high-temperature corrosion-resistant material.

In order to study the structure and properties of alloys of the ternary system Nb-Mo-V , we smelted 29 alloys of the ternary system and 28 of the binary system which had already been studied with metals of varying purity. For the blending of the alloys we used metalloceramic niobium (purity degree 99.9°) and molybdenum (purity degree 99.99°) as well as carbothermic vanadium (purity degree 99.[illegible]) containing 0.06% C and 0.06% S. The rest were metallic admixtures and gases. The alloys were smelted in an arc furnace with a permanent tungsten electrode on a water-cooled [illegible] in a medium of purified helium. Each alloy was [illegible] jected to five-fold remelting (with rolling over) in order to obtain a homogeneous composition. The alloys thus obtained were weighed and compared by weight with the theorectical composition of the charge; if the loss of weight did not exceed 0.3 to 0.4%, a chemical analysis was not carried out. In all the other cases the alloys were [redacted] subjected to chemical analysis. The alloy compositions are shown in the table.

All of the alloys were metallographically investigated in a cast and annealed state. Etching of the alloys by niobium [redacted] and vanadium was effected by a mixture of hydrofluoric acid and nitrous acid, while etching by molybdenum was carried out with a mixture of nitrous and sulfuric acids. Following are the [redacted] etching reagents we selected for the alloys of ternary systems: for the niobium and vanadium angle they consisted of mixtures of hydrofluoric and nitrous acids characterized by a varying ratio of their components, while for the molybdenum angle they consisted of various mixtures of nitrous and sulfuric acids.

All [redacted] of the cast alloys of the systems Nb-Mo, [redacted] Nb-V and Mo-V had monophase structures similar to the structure of an alloy with 50% Nb and 50% V in the system Nb-V, 60% Mo and 40% V in the system Nb- V and with 89.7% Nb and 10.3% Mo in the system Nb-Mo (Figs. 1, a b, c).

The cast alloys of the ternary system also had a monophase structure, but most of them revealed a dendritic liquation (Fig. 1, d, e,f).The alloys were subjected to a protrac[redacted] anneal at 1000° during 300 hours. Investigation of the microstructure of the annealed [redacted] alloy showed that the alloys of binary and ternary systems were monophase and that a dendritic structure was hardly detectable in them (Fig. 1, g, h, i).

For all the alloys of the ternary system and the three binary systems, the solidus temperatures were measured. The determination was carried out with the drop method by sealing the opening (0.7 to 0.8 in diameter and 2.5 to 3 mm in depth) on the specimen in the form of small rods 4 x 4 x 10 mm in size clamped by tungsten electrodes and connected with water-cooled copper bands.

Fig. 1 . Microstructure of binary and ternary alloys of the system Nb-Mo-V, cast (a-β) and annealed [redacted] at 1000° during 200 hours [illegible].

Fig. 2. Curves of fusibility and properties of Nb-Mo, Mo-V, and Nb-V alloys; H_B - Brinell hardness, kg/mm^2, V - oxydation rate mg/cm^2 hour.

The temperature was measured by means of an optical pyrometer calibrated for pure metals: Mo, Nb, V, Zr, Ti and Ni. The Table and Fig. 2 show the solidus temperatures and the fusibility curves of three binary systems. It must be pointed out that the trend of the solidus curves of the fusibility diagrams of the systems Nb-Mo, Nb-V and Mo-V is similar to the one obtained earlier (1-3), with the difference that in the Nb-V system the minimum temperature is somewhat lower and corresponds to 1720° which is due to the fact that in the present work we used carbothermical instead of calcium-thermical vanadium. In the Nb-Mo system, minimum temperatures differ somewhat from those obtained earlier with carbothermic materials and amount to 2290°, thus corresponding to alloys containing 30 and 45° Mo. In the Mo-V system, all the solidus temperatures are higher than those established earlier, when we used aluminum-thermic vanadium with a purity degree of 95.5%, which contained many admixtures.

The melting points of the alloys of the ternary system are also shown in the Table. The structure diagram for Nb-Mo-V is plotted on the basis of measurements of the melting points of alloys and investigations of the microstructure of cast and annealed alloys. Figure 3 shows the projections of solidus isoterms on concentration triangle of the system Nb-Mo-V and the fusibility diagrams of binary systems. The melting points of ternary system alloys drop from alloys containing great quantities of molybdenum (2450°) towards alloys containing great quantities of vanadium (1800°).

Structure Diagram of Alloys of the System Niobium-Molybdenum-Vanadium

1) composition, weight, % 2) H_B, kg/mm^2 3) t_f % °C 4) oxidation rate, mg/cm^2 hour at °C 5) ● overweight 6) ● weight loss 7) ● overweight 8) ● weight loss.

Fig. 3. Projection of solidus isoterms on the concentration triangle (weight, %) of the Nb-Mo-V system and fusibility diagrams of binary systems Nb-Mo, Mo-V and V-Nb.

The trend of solidus temperature curves on the plotted vertical sections with a constant content of molybdenum equalling 85, 75, 60, 45, 30 and 15 % weight (Fig. 4a) and a constant niobium content equalling 55, 40, and 25% weight (Fig. 4b) reveals the presence in the ternary system of an uninterrupted series of solid solutions: the curves are gradually dropping as the vanadium content increases.

The cast and annealed [redacted] alloys were tested for Brinell hardness with a KhPO-250 device with a stress of 250 kg/mm^2 and a ball diameter of 5 mm. The results are shown in the table and also in Fig. 2 (for the binary systems also in Fig. 4a,b). For the vertical sections of the ternary system mentioned. The hardness of alloys after annealing [redacted] at 1000° during 300 hours dropped considerably, for some alloys by more than 100 units. The hardness of niobium amounted to 114 to 107 kg/mm^2. This made it possible to roll it cold into a thin foil and even draw it into a wire, when cast, without intermediate anneals [redacted]. Binary niobium alloys containing 4.71% Mo and 2.4% V, underwent cold treatment successfully.

The hardness of binary and ternary alloys changed in accordance with the formation of an uninterrupted series of solid solutions over the entire range of concentrations. Hardness of ternary alloys lying on sections which are parallel to the niobium-vanadium side, with a constant molybdenum content, is expressed by convex curves (Fig. [illegible]a); the hardness numbers increase as the vanadium content increases, [redacted] attain their optimal magnitude and then decrease.

Fig. 4. Vertical sections of Nb-Mo-V system with constant molybdenum and niobium content and alloy properties; H_B - Brinell hardness, kg/mm^2; v - oxidation rate, mg/cm^2 hour.

Alloys containing 32.2% Mo; 26.3% V, 41.3% Nb, have the greatest hardness (410 kg/mm^2). Hardness variation of alloys with constant niobium content (Fig. 4b) is expressed by similar curves. From the lines of equal hardness shown in Fig. 5 it can be seen that the greatest hardness increase takes place approximately in the central part of the diagram. Alloys based on niobium were the softest alloys.

Fig. 5. Lines of equal hardness of Nb-Mo-V system alloys.

We investigated the oxidizability of all the ternary alloys and corresponding binary alloys at 1000 to 1200°. For this purpose we took specimens 4.5x4.5x10 to 8 mm. They were placed into porcelain crucibles, which were calcinated beforehand to a constant weight, and were held in the furnace with air at temperatures ranging from 1000 to 1200° for one hour. The specimens were weighed [redacted] separately and together with the crucibles, prior to and after holding. The oxidation rate was determined by overweight and by weight loss, the latter procedure being more convenient for alloys rich in molybdenum and vanadium since their oxides are volatile. The oxides and sinter [redacted] were removed mechanically: by scraping off and polishing with paper. The results are shown in the Table and in Figs. 2, 4.

The investigations have shown that alloys with 4.7. and 6.7 % weight Mo as well as alloys containing 4.6 and 5.6% weight V have the lowest oxidation rate [redacted] at 1000° (by overweight and by weight loss). In the case of alloys containing large quantities of molybdenum and vanadium, the oxidation rate increases considerably. Somewhat lower is the oxidizability of alloys with 60 and 75% weight V, although it is still comparatively high (Fig. 6). Oxidizability -

the Mo-V system does not change substantially and remains very high both at 1000 and 1200° since on the surface of most Mo-V alloys unstable low-melting oxides are formed.

At 1200°, the alloys with the highest degree of oxidation resistance were found to be niobium alloys with 15.4% weight Mo and 2.4% weight V. As the molybdenum and vanadium content grew, oxidation resistance decreased considerably. The increased oxidation resistance observed in niobium alloys containing small quantities of molybdenum and vanadium is apparently due to the capacity of the above alloying elements to substitute the niobium atoms in the oxide film Nb_2O_5 thus improving its mechanic stability. An increase in the molybdenum and vanadium content results in an abrupt deterioration of oxidation resistance since the propective films lose their stable properties because of the beginning formation of liquid oxides of these metals. Thus, for example, in alloys containing 25% weight V, at 1000° a liquid component appears in the oxide film. It should be noted that oxidizability of binary alloys containing over 20% weight molybdenum and from 18 to 55% weight vanadium is better at 1200° than at 1000°, which may possibly be the result of the thickening of the film at increasing temperatures.

We investigated the oxidizability of all the ternary alloys (Table, Fig. 4a, b). Of all the alloys investigated, niobium alloys with 5% Mo, 2.8% V and 5% Mo , 5.6% V showed the highest oxidation resistance at 1000° and 1200°.

Attention should be devoted to the fact that an impoved high-temperature corrosion resistance of ternary niobium alloys was observed at a lower alloying percentage than in the case of binary alloys. It has also been observed that the oxidation rate of ternary alloys is occasionally higher at 1000° than at 1200°.

Conclusions. On the basis of investigation of microstructures of cast and annealed alloys, their hardness and the determination of their melting point, we plotted the structure diagram of the system Nb-Mo-V and checked the corresponding binary system, investigated earlier, against metal of identical purity.

We established the existance in the Nb-Mo-V of an interrupted zone of solid solutions.

We plotted the isothermal curves of solidus temperatures which show that the melting point of alloys drops (from 2550 to 1800°) as their vanadium content increases.

Alloys of the niobium angle were characterized by the lowest hardness (105 to 220 kg/mm^2).

After investigating the [redacted] oxidizability we found that the alloys with the highest high-temperature [redacted] corrosion resistance were niobium alloys with the following composition: in binary systems at 1000° - alloys with approximately 5% Mo and 5% V; at 1200° - with [redacted] 15.4% Mo and 2.4% V; in ternary systems - alloys with 5% Mo, 2.8% V and 5% Mo, [redacted] 5.6% V . Moreover, these [redacted] alloys turned out to be technologically most effective.

All the other alloys with high molybdenum and vanadium content had high oxidation rates.

The change in hardness as a result of the composition of binary and ternary alloys corresponded to the properties characterising uninterrupted series of solid solutions. Changes in high-temperature [redacted] corrosion resistance as a result of the composition were not depending on any such factors.

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