STRUCTURE CHARACTERISTICS AND SUPERCONDUCTING PROPERTIES OF TITANIUM-NIOBIUM ALLOYS

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The niobium-titanium system is a basis for development of the superconducting alloys with high critical and technological parameters. Further developments of titanium-niobium alloys depend on favourable combinations of three factors: (1) high basic superconducting properties (H_{c2}, T_c) typical of body centered cubic solid solution, (2) good manufacturing properties of the alloys, and (3) the possibility of controlling the structure and consequently the critical current density (J_c) due to the decomposition of body centered cubic solution.

Niobium with titanium forms an β-isomorphous type phase diagram characterized by continuous solid solubility between niobium and the body centered cubic phase of titanium (Fig. 1). The phase α /α +β transformation temperature decreases when niobium is added to titanium [1-3] . For stabilizing the β-phase of titanium below room temperature 23 at.% (36 mass.%) Nb is required. For this content the β /α +β temperature of is equal to 670°C (Fig. 1). The phase transformations in titanium-niobium alloys (as also in other titanium alloys) depend not only on the composition of alloys, the content of impurities present in them, but also on heat treatment temperature, cooling rate, previous mechanical treatment of the material. In [4] it is shown that several martensite phases are formed in titanium based alloys after water quenching from 1000°C. The phase regions according to [5] , are shown in Fig. 1b. The phase boundary $\beta+\omega/\beta$ is shown according to [4] .

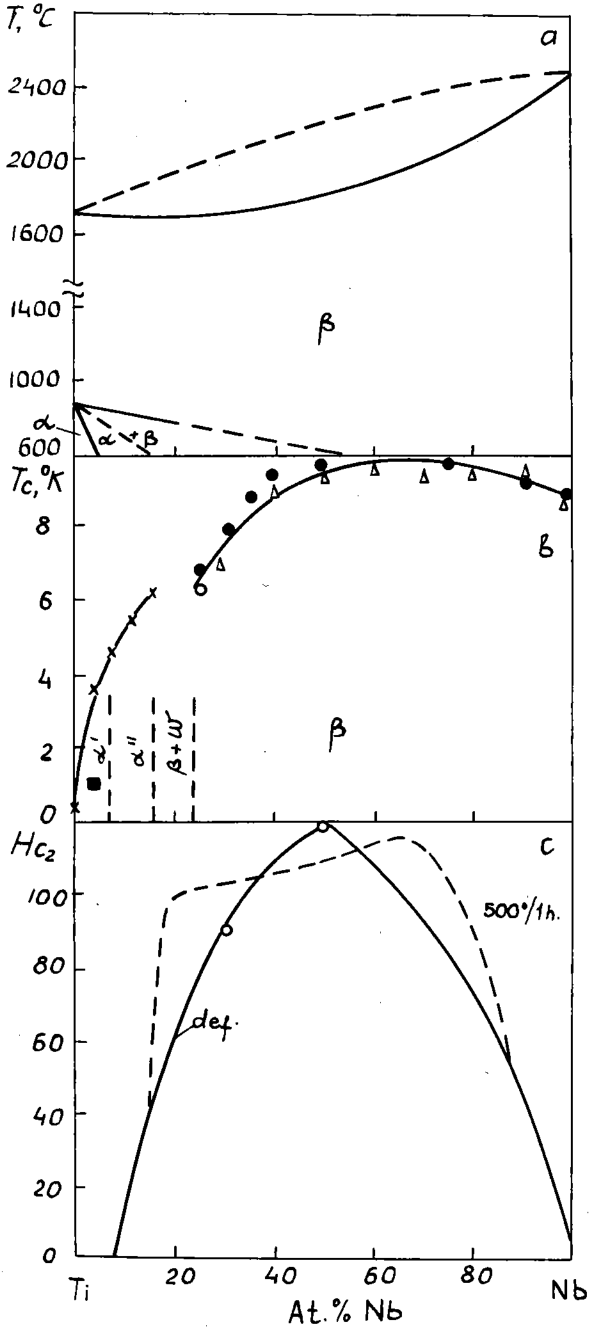

Fig. 1. The phase diagram of the Nb-Ti system (a), T_c, H_{c2} as a function of composition (b, c)

The variation of T_c as a function of concentration is shown in Fig. 1b [5-9] . The body centered cubic solid solution in the system has the highest transition temperature. Maximum value of T_c comes to 10K at 50 at.% Ti. For the α phase containing about 2.5 at.% niobium (annealed at 650° for 2 hours) T_c is equal to 1.5K [9] . An increase in the content of niobium in α -solid solution due to quenching and appearance of martensite phases result in the increase of T_c (Fig. 1b).

It was difficult to determine the transition temperature of ω -phase as it (the ω -phase) is always found in combination with body centered cubic solid solution, and often in a finely dispersed state. Besides, it must be noted that its composition varies depending on formation conditions. Therefore, the estimated values of T_c for ω -phase vary slightly.

In [10] it is pointed out that T_c of ω -phase for the Ti-17 at.% Nb alloy does not exceed 3.8K, but because of the proximity effect the critical temperature of the phase in the case of finely dispersed distribution may attain a value of more than 4.2K.

In Fig. 1c the concentrational dependence of upper critical magnetic field (H_{c2}) is shown. An upper critical magnetic field depends mainly on T_c, residual electric resistivity and specific heat. In the niobium-titanium system the concentrational dependence of H_{c2} is close in character to the T_c dependance on composition. Maximum value of H_{c2} for quenched and deformed alloys corresponds to 50 at.% Ti. If a body centered cubic solid solution decomposes accompanied with the precipitation of the α -phase and enrichment of solid solution by niobium, the critical field of such alloys increases [11] . Thus, the compositions of the alloys with a high critical field increase in area as shown in Fig. 1c.

The critical current density differs from first two characteristics and depends not only on the composition of alloys, but also on their structure. By changing the structure of alloys the critical current density may be varied by several orders. For example, the critical current density of niobium single crystal containing 63 mass % Ti is equal to 10^2 A/cm^2 and of the specimens with two phase structure is equal to 10^5 A/cm^2. If we take into account that J_c is also related with T_c and H_{c2}, then a complex dependence is obtained. We studied the variation of critical current of the niobium-titanium alloys as a function of concentration. The alloys were investigated in the deformed state in magnetic fields ranging from 25 to 5 Koe (Fig. 2). It is evident that the maximum of J_c shifts towards niobium-rich alloys. As the field increases the maximum values shift towards the alloys rich in titanium characterized with higher critical fields. Starting from 60 at.% Nb alloys an increase in J_c is being observed. This curve to some extent repeats in character the hardness curve shown in [9] . Such an increase is related to the predecomposition state that appears in a solid solution when the composition approaches β-solid solution boundary at room temperature. These data reveal that J_c is sensitive to the structural state of alloys. In the system niobium-titanium are used alloys containing 60-78 at.% Ti on the base of a body centered cubic solid solution with high initial characteristics of T_c, H_{c2} and good mechanical workability. This does not exclude the use of other alloys for more specific purposes.

Depending on mechanism of the magnetic flux pinning the alloys can be divided into two groups: 78-65 at.% Ti and 65-50 at.% Ti, although no distinct boundary exists between them. Low transition temperature of α-phase makes it possible to use the phase precipitates for nucleation of the pinning centers in group I alloys. In group II alloys the formation of the cellular structure is a preferable mechanism for increasing J_c. The mechanisms of increasing J_c mixed in character are used for magnetic flux pinning at the boundary of these groups.

The decomposition of β-solid solution proceeds according to a general scheme characteristic for isomorphous solid solutions and substantially depends on composition and annealing temperature [3] . Not only the α-phase but also the ω-phase, although it has higher T_c, can also be used to increase critical current.

For a niobium alloy containing 75 at.% Ti the critical current rises with the increasing of annealing temperature and

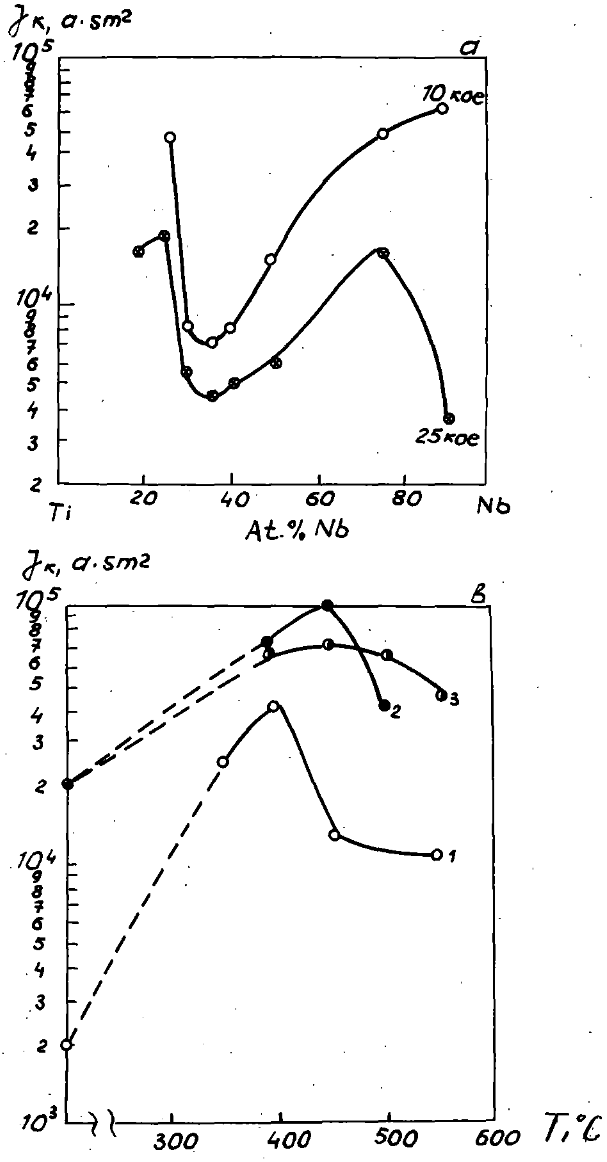

Fig. 2. Critical current the Nb-Ti alloys: (a) J_c - composition (1 - after 10 kOe, 2 - after 25 kOe); (b) J_c - heat treatment Ti-25 at.% Nb alloy (1 - annealed, 2 - deformed, 3 - plastic deformation after annealing).

passes through the maximum at 400-450°C (Fig. 2b). Such a shape of the curve is associated with the formation of optimal structure of alloy.

In Fig. 3 the structure of the titanium-25 at.% Nb alloy after annealing at 450°C for 3 hours is shown. It is seen that α - phase precipitates have different sizes. In dislocations clusters the α -phase particles of several thousand Å, and, in other place smaller particles of 300x100 Å grow up [12] . Thus it is possible to increase critical current from 10^3 up to 10^5 A/cm^2 by means of heat treatment [13-18] .

Thus, even plastic deformation which is a necessary step in manufacturing of the superconductors results in the appearance of structural microinhomogeneties. It must be added the inhomogeneties caused by segregation, different orientations of grains, etc., which lower critical current in industrial materials by no less than an order. It is possible to get rid of such defects in a structure by increasing significantly J_c, which can be increased by using modern metallurgical technology.

In group II alloys the cellular structure created by specific thermal treatment acts as pinning centers. In [19] it is shown for the Nb-60 at.% Ti alloy that Lorentz force (F) which determines the value of critical current depends on cell size. With the decreasing of the cell size from 2000 Å to 500-400 Å the Lorentz force increases. When annealing is produced below 385°C the cell size does not increase, but the Lorentz force increases. For this reason it appears to the authors that the subcells of 100-200 Å size are responsible for the additional increase in F. The precipitation of excess phases along the dislocation lines should be also taken into consideration. It is proved also by the fact that α -phase was found in this range of concentrations [20] .

In the alloys, in which the second phase plays a leading role in increasing J_c, the phase precipitation process is followed by rearrangement of the dislocation structure. This makes additional contribution to the J_c increse at the boundary of earlier

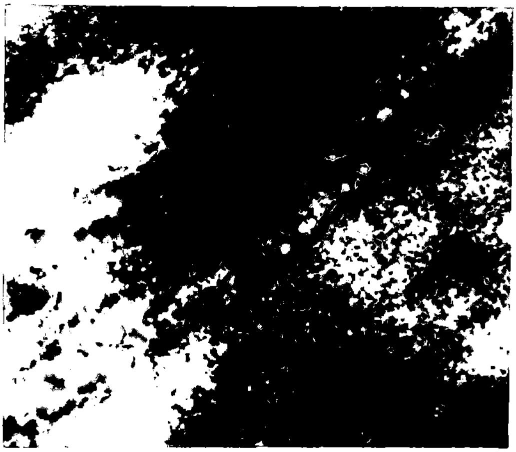

Fig. 3 Microstructure of the Nb-75 at.% Ti alloy (a) deformation 99.9, annealing at 450°C 5 hours, x 60,000.

mentioned groups of alloys. As a result it is difficult to give preference to any mechanism for increasing J_c.

Except heat treatment methods a possibility exists for increasing superconducting critical characteristics by alloying binary titanium-niobium alloys. The selection of alloying element in each case depends on the purposes assigned. However, two basic directions can be pointed out.

<u>First direction</u> - improvement of fundamental properties of alloys, T_c and H_{c2}: second, increase of critical current.

In the first case, since β-solid solution is responsible for high T_c and H_{c2}, transition metals of IVA-VIIA subgroups (Zr, Hf, V, Ta, Mo, W, Re) forming wide ranges of solid solutions with niobium-titanium alloys are used as basic alloying components. The studies of ternary systems with the elements listed above enabled us to establish that T_c of niobium-titanium alloys could be increased by alloying with Zr [21-22] . The increase in critical field is achieved in the system Nb-Ti-Ta. In this system the maximum H_{c2} value is equal to about $\approx$ 124 kOe compared with 117 kOe for binary alloy. In short, moderate success is achieved.

Second direction - alloying is used for increasing critical current of alloys. Several papers dedicated to this problem are available. Based on them the following conclusions can be made. Transition metals - β stabilizers - which form solid solutions lower J_c of niobium-titanium alloys, even if they raise the critical temperature of the alloys The β stabilizers stimulating eutectics formation increase critical current of niobium-titanium alloys due to the precipitation of excess phases characterized with low-temperature T_c [23] .

Zr (neutral element) affects J_c is a different way. Introduction of zirconium into titanium-rich alloys (75 at.% Ti) lowers J_c, while in the alloys containing 60-65 at.% Ti J_c rises with the introduction of Zr. In Japan, industrial superconducting alloys based on ternary system Nb-Ti-Zr have been developed [24] . Probably, hafnium affects differently. Alpha-stabilizers are the most prospective elements from the view point of raising critical current as they shift the range of ($\alpha + \beta$) decomposition in the direction of alloys rich in niobium.

But Al (substitutional solid solutions) lowers J_c [10] . Out of alpha-stabilizers - interstitial impurities - the effect of oxygen has been studied. Data are available which indicate that oxygen increases J_c of titanium-niobium alloys under definite annealing conditions [25,26] . But J_c decreases due to mechanical work the decrease being followed by lowering of T_c and H_{c2}. Although it is possible to raise J_c by heat treatment, this positive effect is mainly characteristic for alloys containing 50-65 at.% Nb. It may also be mentioned that the increasing of the annealing temperatures may result in growth of the precipitates and the degradation of critical current for large articles in particular.

Thus, from the consideration of concentrational and structural dependences of superconducting properties (T_c, H_{c2}, J_c) of niobium-titanium alloys, it is evident that their properties are affected not only by their composition but also the structure depending on the heat treatment. The results of the heat treatment are closely connected with the physico-chemical nature of these materials.

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