FIELD ION MICROSCOPIC STUDY OF THE MICROSTRUCTURE OF SUPERCONDUCTING DEFORMABLE NIOBIUM ALLOYS

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The structure of the Nb-Ti (60 at.% Ti) is studied with a resolution of less than 3 Å after cold deformation and various heat treatments. The presence of a developed system of highly dispersed filamentary zones enriched in niobium is established. In an alloy subjected to cold deformation the transverse dimensions of the zones are ~ 10 Å, the depth exceeds 10^3 lattice constants. During thermal treatment the filamentary zones form plaits with cross sections of $(3-5) \times 10^2$ Å. A structure consisting of filaments measuring 20–50 Å corresponds to treated material with maximum critical parameters. The results confirm the assumption previously suggested that the high current-carrying properties of the alloy are due to layers of niobium or to a phase with a composition close to that of niobium, precipitated as a result of heat treatment and forming a space lattice.

DEFORMABLE alloys based on niobium, namely the ternary Nb–Zr–Ti and especially the binary Nb–Ti, are so far the main material for the preparation of superconducting solenoids both for laboratory applications, with small volume with fields up to 119 kOe[1], and especially for very large volumes and relatively weak fields[2]. The parameters of these alloys are quite high; e.g., for the alloy Nb + 60 at.% Ti we have $T_{cr} = 9.6°K$[3] and $H_{cr} = 145$ kOe (at T = 2°K)[4]; the critical currents are also large. To explain the nature of their high current-carrying capacity and the possibility of increasing it further, it is very important to know the fine details of the structure of these alloys in the form of wire prepared by deep cold deformation and subsequent optimal heat treatment. In cast form, these alloys are not in equilibrium, since they reveal when cooled to room temperature the BCC structure possessed of the Nb–Ti system in the region from the solidification temperature (~ 2000°C) to 883°C, at which the lattices of the components are very close to each other. Below 883°C, a transition takes place in titanium, whose structure changes from BCC to hexagonal. A number of studies, both by electron microscopy[5] and by methods that determine more directly the "superconducting" structure of the alloys (ferromagnetic decoration)[6] have shown that the factors responsible for the high current density are apparently the very dense thin three-dimensional mesh made up by intersection of the slip bands produced by cold deformation, and its decoration by niobium or by a phase with a high niobium content during the heat treatment. According to these investigations, the thickness of the filaments or films of this mesh, which is extremely textured by rolling, is very small and amounts from several dozen to several hundred Angstrom units.

It was thought that the method of field-ion microscopy (FIM) with its tremendous resolution (<3 Å) and its possibility of investigating the object layer by layer will greatly supplement this picture from the quantitative point of view. We report here the results of such investigations on an alloy of Nb + 60 at.% Ti, in the form of wire samples of d = 0.22 mm in various states, viz., initial (after cold rolling) $J_{cr} \approx 15$ Å in a field H = 60 kOe, after optimal heat treatment (400°C two hours), corresponding to the maximum value of the critical current $J_{cr} \approx 30$ Å, and after a heat treatment (550°C, two hours) when the critical current drops to the initial value.

The investigation was carried out in a helium field ion microscope with nitrogen cooling[7] on needle-like samples with initial radius of curvature at the tip ~ 200 Å and with a cone angle 6° ± 3°. It is known that in field-ion microscopy investigations of alloys one encounters serious difficulties connected with the fact that the presence of impurity atoms, and particularly their irregular disposition, leads to a random distribution of material regions that evaporate easily in the electric field necessary to obtain the image. Satisfactory images were obtained so far for the ordered alloys Pt–Co[8] and Mo–Ni[9], and also for alloys that are quite stable in a high-intensity electric field, such as W–Re[10] and W–Mo[11]. The system Nb-Ti, as well as Nb–Zr–Ti, comprises disordered alloys made up of components that are not resistant to evaporation in an electric field. It was therefore necessary to take measures to reduce the exposure time with the aid of an electron-optical converter.

The images obtained on the microscope screen have an irregular form (in the sense of the crystallographic structure) and consist of points of varying size and in brightness, identified as the images of single or several atoms of different components. It is possible to observe clearly on the image the presence of individual sections with large concentrations of bright points, surrounded by regions that are either completely dark or consist mainly of points of low brightness producing a weak background. The images of the samples prepared of an alloy subjected to different processing are significantly different.

In the case of the cold-deformed alloy, one observes clusters of bright points with transverse dimensions of approximately 10 Å, representing the images of one of

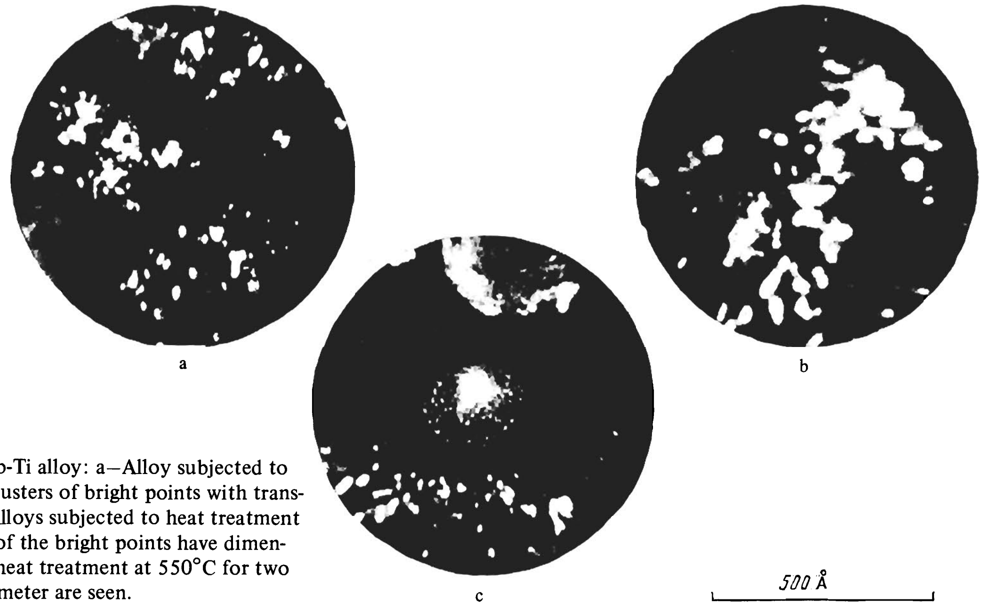

FIG. 1. Field-ion microgram of Nb-Ti alloy: a—Alloy subjected to deep deformation in the cold state. Clusters of bright points with transverse dimensions ~10Å are seen. b—Alloys subjected to heat treatment at 400°C for two hours. The clusters of the bright points have dimensions 20—50Å. c—Alloy subjected to heat treatment at 550°C for two hours. Individual zones of ~300Å diameter are seen.

the alloy components having the brighter reflections (Fig. 1a). The character of the image does not change when several hundred atomic layers are removed one by one from the material, i.e., the indicated clusters have the form of thin filaments that are approximately parallel to the axis of the sample. The alloy heat-treated at 400° C has larger bright zones with diameter up to 20—50 Å (Fig. 1b). The size distribution of the brightly emitting zones is shown in Fig. 2. The question of the distribution of the described filaments in a wire sample of 0.2 mm diameter could not be answered. All the samples were chosen from the central part of the section, since the samples were prepared by electrochemical polishing of the initial wire. With respect to the central part of the wire it can be stated that the indicated sections with the brighter reflections have an average density 10^{11} cm^{-2}.

After heat treatment at 550°C, the picture consists mainly of large bright clusters with dimensions 300—500 Å and with approximately the same distance between clusters. These light clusters consist in turn of smaller sections (Fig. 1c). The zones penetrate very deeply and can be traced to distances of at least a thousand atomic layers. Thus, the investigated samples consist of long filaments of one phase (bright regions) imbedded in the matrix of the other phase. The filaments are approximately parallel to the axis of the initial wire.

An analysis of the field-ion micrograms, the data on the evaporating fields of n-fold ionized atoms of each component of the alloy (Table) calculated from the expression for the evaporating field F of the metal at T = 0°K[12], and a comparison of the field-ion micrograms of the alloy and of pure niobium allows us to conclude that the observed bright spots are images of single atoms of niobium or of their clusters, while the darker ones are titanium atoms. Indeed, it is seen from the table that the niobium atoms are evaporated by the field of higher intensity than the titanium atoms. Consequently, at one and the same value of the field intensity the titanium atoms will be evaporated more rapidly than the niobium atoms. As a result, the sections with the larger concentration of the niobium atoms project over the common surface, and the local field intensity over them is accordingly higher. As already noted, in the working regime and at the best-image field, the niobium atoms are also evaporated quite rapidly, but the titanium-atom evaporation will always lead.

We note that in addition to the described typical picture of the images, in some of the samples of the initial material (in 5 out of 60 cases) there were observed inclusions of practically pure niobium. Such images sometimes appear after microexplosion of the sample by the field. The transverse dimensions of the inclusions were 200—300 Å (Fig. 3a). For comparison, Fig. 3b shows the field-ion picture of a niobium tip.

The purity of the material can be assessed from the largest Miller index contained in the designation of the atomic plane formed by the electric field and revealed on the field-ion image. The purity of the material is connected with the maximum Miller index (H_*) by the relation[13]:

$$C_{met} = 1 - h_*^{-3}. \quad (1)$$

Since the image of the niobium shows the (150) face, it

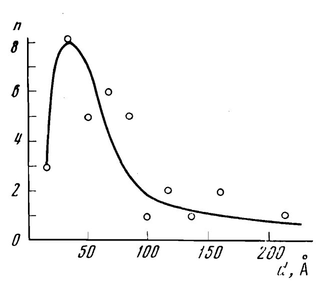

FIG. 2. Distribution of the dimensions of the brightly emitting sections of an alloy subjected to heat treatment (two hours) at 400°C.

Metal	Intensity of evaporating field, MV/cm			
	F^0	F^+	F^{++}	F^{+++}
Nb	660	800	350	510
Ti	400	520	280	460

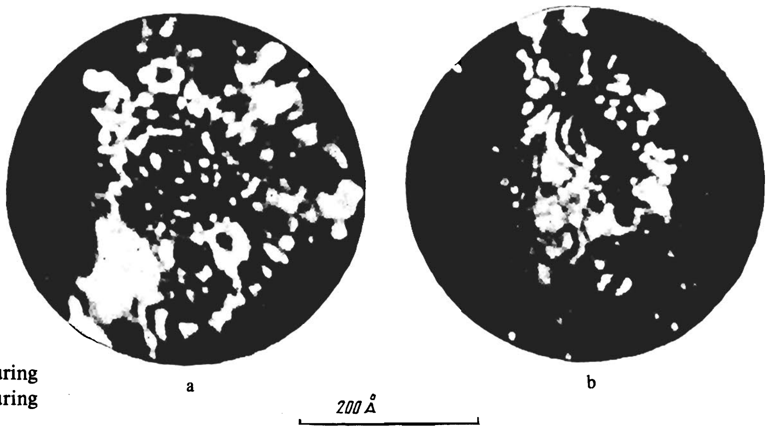

FIG. 3. a—Field ion microgram of a section of an alloy measuring ~300Å, containing ~96.3% Nb. b—Microgram of a section measuring ~300Å of the surface of Nb 99.2% pure.

follows that according to (1) the niobium concentration of the sample at our disposal (Fig. 3b) is 92.2%. The niobium concentration in the region of the inclusion (Fig. 3a), corresponding to a displayed face (321), is 96.3%. In other cases, the purity of the inclusions in the initial materials is estimated at 98.5%, when the planes (141) are revealed. Thus, the results show that the investigated wire made of deformed alloy based on niobium constitutes from the microstructure point of view an alloy matrix threaded by filament-like precipitates of a phase that is close in composition to pure niobium. This confirms the representation of the current-carrying system of these superconducting alloys, according to which the metastable niobium alloy becomes threaded-through after strong plastic deformation (rolling in the case of a wire) and subsequent heat treatment, by a three-dimensional filament-like system of niobium (or of a phase close to pure niobium), precipitated from the three-dimensional grid of the tracks of plaiting of dislocations and slip bands.

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