# *INFLUENCE OF THE STRUCTURAL STATE ON THE SUPERCONDUCTING PROPERTIES OF ZIRCONIUM ALLOYS CONTAINING 20 to 25% NIOBIUM*

Yu. F. BYCHKOV, I. N. GONCHAROV, and I. S. KHUKHAREVA

Joint Institute for Nuclear Research

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The influence of the structural state on the superconducting and mechanical properties of alloys is investigated in detail (the following properties were measured: electrical resistance, critical temperature, dependence of the critical current density on the angle between the magnetic field and the plane of rolling, ultimate tensile strength, hardness, relative elongation as a function of the temperature of one-hour annealing). The most interesting properties were observed in the region of precipitation of the $\alpha$-phase or metastable $\omega$-phase (high values of $j_c$; also in the latter case there is almost complete absence of current anisotropy). A qualitative explanation of the results is presented on the basis of the Anderson model. It is shown that $j_c$ may increase even for a decrease in the number of dislocations or vacancies, provided other mechanisms exist for stabilization of the current. A relation was observed between the variation of $T_c$ and decomposition of the $\beta$-solid solution during the annealing.

THE first investigations of the properties of zirconium-base alloys containing 20 to 25% niobium, after cold deformation and also after certain kinds of heat treatments, showed that they possess a rather high critical current density ($j_c$ is less than $10^4$ A/cm$^2$ at 20 to 30 kG[1-3]). However, since the critical current density is a structure-sensitive property, and in zirconium-base alloys it is possible to obtain a considerably larger variety of structural states than in alloys containing a large amount of niobium, it seemed to us advisable to study in more detail the influence of different metallurgical factors on the superconducting properties of alloys containing 15 to 25% niobium. In these alloys one can, in particular, use such a powerful mechanism for altering the properties as precipitation of the finely dispersed particles of the transitional $\omega$-phase.

Zirconium-base alloys are also of interest because, according to the results of investigations in pulsed magnetic fields,[4,5] the upper critical field in the zirconium-niobium system has a maximum value (125 to 150 kG) near 25% niobium content.

## 1. INFLUENCE OF STRUCTURE ON THE CRITICAL CURRENT DENSITY

Thermomechanical treatment enables us to strongly increase the critical current density in alloys of zirconium containing 20 to 25% Nb. As previously communicated by us,[6,7] one hour's intermediate annealing of an alloy containing 20 to 25% Nb in the region of precipitation of the $\omega$-phase (400 to 450°C) and at a somewhat higher temperature in conjunction with subsequent rolling from 1 to 0.05 mm, leads to an increase of $j_c$ (27 kG) by 20 to 30 times. In this connection, the dependence of the critical current on the applied magnetic field becomes very weak.

With variation of the temperature of the intermediate annealing in the region from 400 to 550°C, $j_c$ changes comparatively monotonically, and with regard to the curves showing the dependence of $j_c$ on the annealing temperature, it is impossible to reach any conclusions about whether two different mechanisms for decomposition of the solid solution act in this temperature interval—formation of a transitional $\omega$-phase at 400 to 450° and precipitation of $\alpha$-Zr and of recrystallization nuclei at 500 to 550°. The change in the decomposition mechanism is clearly shown by examination of the influence on $j_c$ of the orientation of the plane of rolling of the ribbon relative to the magnetic field direction, that is, the anisotropy of $j_c$. As is evident from Fig. 1a, after annealing an alloy containing 20% Nb at 400°C the anisotropy almost vanishes, in spite of the fact that after annealing the samples underwent cold rolling from 1 to 0.05 mm. At lower and higher annealing temperatures, the magnitude of $j_{c\perp}/j_{c\parallel}$ turned out to

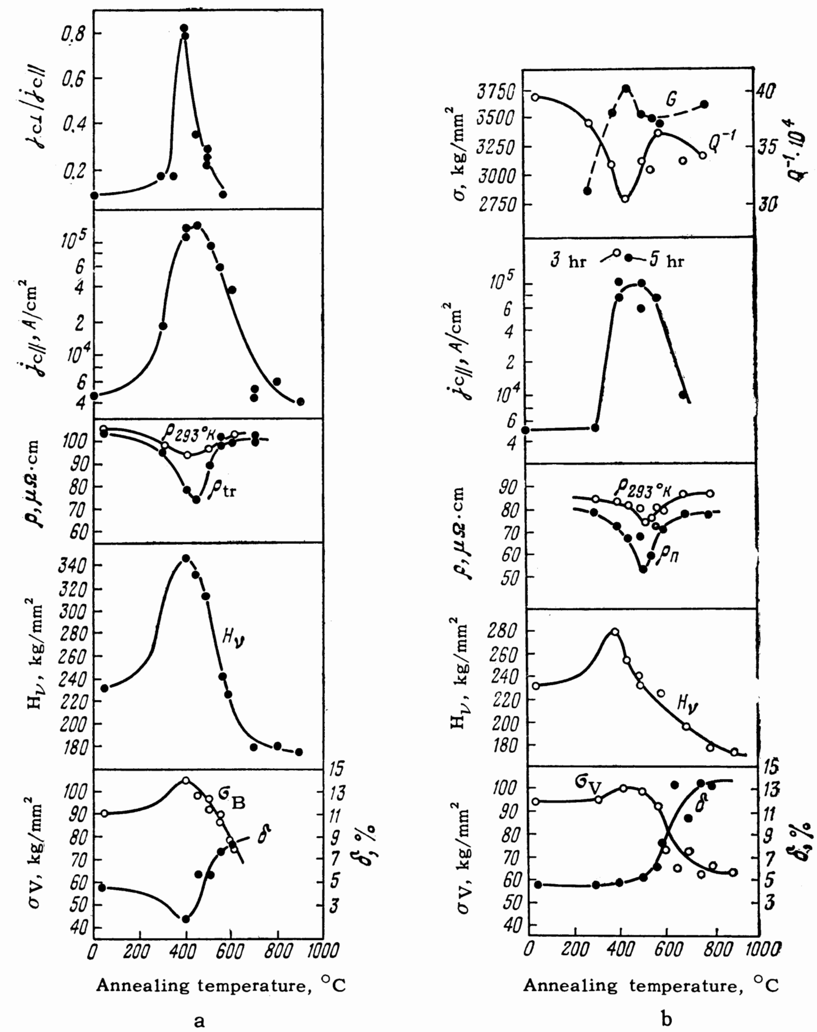


FIG. 1. Physical properties of alloys: a) Nb + 80% Zr; b) Nb + 75% Zr. The anisotropy ($j_{c\perp}/j_{c\parallel}$) of the critical current density in a field of 17 kgauss, the critical current density $j_c$ in a transverse field of 27 kgauss, and the electrical resistivity $\rho$ – after one hour's intermediate annealing of 1 mm thick ribbons with subsequent rolling to 0.04 to 0.05 mm. The other physical properties – after annealing without subsequent deformation. The shear modulus G and the internal friction $Q^{-1}$ were measured for wires of 0.25 mm diameter ($j_{c\perp}/j_{c\parallel}$ – magnetic field, respectively perpendicular and parallel to the plane of rolling).

be 5 to 10 times smaller. Almost the same results were obtained for an alloy containing 25% Nb.

The dependence of $j_c$ on the orientation of the field relative to the plane of rolling is clearly indicated by the great sensitivity of the superconducting current to anisotropy of defects and precipitates. The microscopic structures of a cold-worked alloy differ sharply in planes perpendicular to and parallel to the plane of rolling. Grains are seen in the rolling plane which are elongated in the direction of rolling, whose width almost does not vary as a result of rolling, and inside of which a comparatively small number of dislocation lines appeared. In the perpendicular plane, a large number of layers parallel to the plane of rolling are observed, which become all the more thin and flat with increase of rolling. The temperatures of intermediate annealing at which an abrupt increase of $j_c$ was observed lie considerably below the recrystallization temperatures of these alloys; therefore, changes of the microstructure observable in a metallurgical microscope did not occur. The difference in the microstructures reflects a difference in the distribution of the density of defects along various directions: layers parallel to the plane of rolling contain a large number of defects. It was previously shown [8] that $j_c$ in practice does not depend on the direction of excision of the samples in the rolling plane, that is, the presence of texture along the direction of rolling does not play an essential role.

It is possible to understand the facts described above on the basis of the Anderson theory, [9,10] which gives a rather good description of the current-carrying properties of hard superconductors. If defects (dislocations, inhomogeneities, precipitates, etc.) are present in a metal, then they act as energy barriers which hinder the free motion of magnetic flux bundles [11] having dimensions on the order of the magnetic field penetration depth ($\sim 5 \times 10^{-5}$ for the alloys under consideration). The more such defects along the current line and the more effective their influence, the greater the stabilizing action against the Lorentz force. As is shown in the article by Friedel et al.,[12] optimal conditions arise when the dimensions of the precipitates approach the distance between the current lines, and also in this case the dependence of $j_c$ on the applied field is nearly absent.

Apparently alloys which are annealed at temperatures of 400 to 500° come close to realization of these conditions. From the point of view of this theory it is easy to understand why in cold-deformed alloys $j_{c\parallel}$ has a higher value than $j_{c\perp}$. This is associated with the fact that in the case of parallel alignment of the plane of rolling and the field, the magnetic flux lines lie in planes containing a large number of defects, so that the distances between the energy barriers along the flux line turn out to be small. In the case of perpendicular arrangement of the rolling plane and the field, the flux lines comparatively rarely cross the layers containing an increased number of defects; as a result, the stabilizing action of the latter turns out to be much weaker, and $j_{c\perp}$ is smaller than $j_{c\parallel}$.

Intermediate annealing of alloys at temperatures of 500°C and somewhat above, that is, in the region of precipitation of almost pure $\alpha$-zirconium and embryonic recrystallization, leads to a substantial increase of $j_{c\parallel}$; however, the value of $j_{c\perp}/j_{c\parallel}$ turns out to be nearly as low as for the cold-rolled alloy. This is apparently explained by the fact that the grains of the $\alpha$-phase and the nuclei of the $\beta$-phase are, for the most part, precipitated along the crystal boundaries so that, as a result of the subsequent deformation, plane layers containing an increased number of defects appear.

On the other hand, annealing in the region of precipitation of the $\omega$-phase (400 to 450°C) leads not only to an abrupt increase of $j_c$, but also makes the dependence of $j_c$ on the direction between the field and the rolling plane almost isotropic. This is associated with the fact that precipitation of the $\omega$-phase occurs not only along the crystal boundaries but also inside them, that is, relatively uniformly. It is possible to reach such a conclusion on the basis of direct electron microscope investigations. A uniform distribution of finely-dispersed precipitates is in general characteristic for the processes of decomposition of solid solutions at relatively low temperatures.[13] The size of the $\omega$-phase precipitates, both in Zr-Nb as well as in structurally similar Ti alloys, does not exceed $10^{-5}$ cm,[14] but the $\alpha$-phase precipitates are larger. The particles of the $\omega$-phase essentially do not change their dimensions in the cold-deformation process following the annealing, since they are substantially harder than the initial $\beta$-phase. Their distribution after cold deformation also remains nearly uniform, leading to the absence of appreciable anisotropy of $j_c$.

Thus, the most important consequences of the intermediate annealing of alloys containing 20 to 25% Nb at 400 to 550°C are a sharp increase of $j_c$, a relatively weak dependence of $j_c$ on the external magnetic field, and, in addition, almost complete absence of critical current density anisotropy in the region of precipitation of the $\omega$-phase.

## 2. INFLUENCE OF THE NATURE OF THE DEFECTS ON THE CRITICAL CURRENT DENSITY

In order to determine the nature of the processes occurring in the stage of intermediate annealing of an alloy containing 25% niobium, a measurement was made of those physical properties which are responsive to different types of defects—the internal friction $Q^{-1}$ and the electrical resistivity $\rho$. As is well known, the electrical resistance varies markedly during a change of the concentration of point defects (vacancies and dislocated atoms), and the internal friction is responsive to the density of dislocations.[15] It was found that during annealing at 400 to 500°C a decrease occurred in the internal friction and in the electrical resistivity, especially the residual electrical resistivity, which indicates a decrease in the number of point and line defects during such annealing (see Fig. 1). Since final annealing at 400° without subsequent cold deformation also leads to an increase of $j_c$ by several times, and since the concentration of line and point defects decreases during such annealing, one can conclude that the value of the critical current density in a magnetic field depends not only on the density of line or point defects, but also on other factors. In the present case, apparently the presence of finely-dispersed precipitates, in particular, precipitates of the $\omega$-phase, turns out to have the most influence on the stabilization of $j_c$.

The internal friction $Q^{-1}$ depends significantly on the prior history of the samples: In connection with a measurement of $Q^{-1}$ for a wire containing 25% niobium, but from another batch, lower values were obtained than those presented in Fig. 1b; the cold-deformed wire had $Q^{-1} = 15 \times 10^{-4}$, but after final annealing at 400 to 450° this value decreased to 12 to $13 \times 10^{-4}$. During cold deformation, which was carried out after annealing at 400° for one hour, a considerable increase of the internal friction to the value $19.5 \times 10^{-4}$ occurred, that is, in-

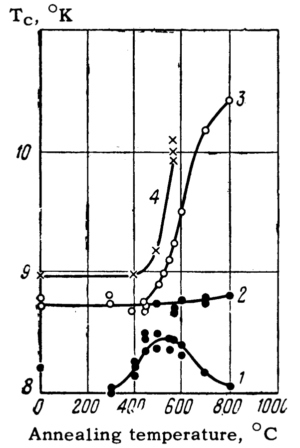


FIG. 2. Dependence of $T_c$ on the temperature of one-hour annealing: 1 – intermediate annealing, ribbon strip, 20% Nb; 2 – intermediate annealing, ribbon strip, 25% Nb; 3 – final annealing, wire, 25% Nb; 4 – intermediate annealing, 0.5 mm diameter wire with subsequent deformation to 0.25 mm diameter, 25% Nb (wire from another batch).

Phase Composition of Alloys after One Hour's Annealing at Various Temperatures

| Annealing Temperature, °C | Niobium Content | |
|---|---|---|
| | 20% | 25% |
| Cold-deformed | $\beta$ | $\beta$ |
| 300 | $\beta$ | $\beta$ |
| 400 | $\beta + \omega\ (\omega \leqslant \beta)$ | $\beta + \omega$ (very small) |
| 450 | $\beta + \omega\ (\omega < \beta)$ | $\beta + \omega$ (very small) |
| 500 | $\beta + \alpha\ (\alpha \leqslant \beta)$ | $\beta + \alpha\ (\alpha \leqslant \beta)$ |
| 550 | $\beta + \alpha\ (\alpha < \beta)$ | $\beta + \alpha\ (\alpha < \beta)$ |
| 600 | $\beta + \alpha + \beta_{Nb}\ (\beta_{Nb} < \alpha;\ \alpha < \beta)$ | $\beta + \alpha + \beta_{Nb}\ (\alpha \sim \beta)$ |
| 700 | | $\beta + \alpha + \beta_{Nb}\ (\alpha \sim \beta)$ |

*The x-ray photographs were taken of the surface of Zr + 25% Nb wires, subjected to final annealing, and of the surface of needle-shaped samples cut out of 1 mm thick sheets (Zr + 20% Nb); $\beta$ – initial $\beta$ – solid solution; $\alpha$ and $\beta_{Nb}$ – the $\alpha$ – zirconium and $\beta$ – phase containing 85% Nb which are formed as a result of decomposition.

termediate annealing apparently increases the capacity of an alloy for the formation of dislocations during subsequent cold deformation.

From Fig. 1 it is evident that in the $\omega$-phase precipitation region the tensile strength $\sigma_V$ of the alloys, and also their hardness $H_\nu$, increases somewhat. With further increase of the annealing temperature, their tensile strength falls, but the ductility $\delta$ increases.

## 3. RELATION BETWEEN THE TEMPERATURE OF TRANSITION TO THE SUPERCONDUCTING STATE AND THE STRUCTURE OF ALLOYS

The critical temperature was determined according to change of resistance: The value of the temperature at which the resistance of the sample $R(T) = 0.5\ R_n$, where $R_n$ is the residual resistance, was taken as $T_c$. The dependence of $T_c$ on the temperature of the one-hour anneal is shown in Fig. 2. It is apparently necessary to explain the difference in character of the curves as due to a different degree and extent of the decomposition of the $\beta$-solid solution occurring in the samples. In the case corresponding to curves 1 and 2, the samples were prepared and treated under the most uncontaminated conditions; as a consequence decomposition, even on the surface, turned out to be very insignificant. As is evident from the table, three phases were observed upon x-ray investigation of the surface of a ribbon strip containing 20% Nb immediately after one hour's annealing at 500 to 600°C: $\alpha$-zirconium, the original $\beta$-solid solution, and a small amount of $\beta$-phase containing 85% Nb. After removal from the surface of this alloy of a $5 \times 10^{-2}$ mm thick layer, the $\alpha$-phase was not observed in Debye patterns, so that in this case appreciable decomposition took place in a very thin surface layer which, during subsequent rolling, was decreased by as much as 20 to 25 times. Possibly the increase of $T_c$ at 0.5°K (curve 1 on Fig. 2) is only associated with the presence of this surface layer since during the measurement, the current flows along the surface of the sample. However, in the depth of the sample, decomposition with precipitation of $\alpha$-zirconium and a corresponding enrichment of the $\beta$-solid niobium solution takes place during such an annealing process. Direct measurements of the lattice parameter for deep layers of alloy containing 20% Nb showed that after annealing at 570°C an increase of the niobium content in the $\beta$-solid solution up to 25% is actually observed. From x-ray crystallographic analysis of alloy containing 20% Nb, annealed at 400°C, it follows that the phase compositions are the same on the surface and in the depth of the sample and represent the $\omega$-phase and a somewhat enriched niobium $\beta$-phase.

Concerning the absence of any noticeable variation of $T_c$ upon annealing ribbon strips containing 25% Nb (curve 2 in Fig. 2), then, possibly here the decomposition took place in an even thinner layer which was removed during the preparation of samples for measurements, but it absolutely did not take place in the depth of the sample (x-ray structural analysis did not reveal changes of the lattice parameter or the appearance of new phases).

The sharp increase of $T_c$ for wire samples containing 25% Nb, subjected to final annealing at 500°C and above (curve 3 on Fig. 2), is undoubtedly connected with decomposition of the solid solution into $\alpha$-zirconium and a $\beta$-phase containing 85% niobium, having $T_c \sim 11$°K (at 700 and 800°C the decomposition occurred, obviously, in the process of cooling the samples, when their temperatures were on the order of 500 to 600°C). In the case of wires, decomposition generally took place at a considerable depth from the surface. Thus, after removing from the wire, subjected to final annealing at 600°C, a 0.05 mm thick layer the critical temperature decreased from 9.6 to 8.9°K. On another batch of wire on which intermediate annealing at 570°C was carried out on 0.5 mm diameter wire with subsequent rolling to 0.25 mm, the removal of a 0.035 mm layer absolutely did not change $T_c$ ($\approx 10$°K).

Increase of the duration of the anneal was also accompanied by an increase of the critical temperature. For strips of alloy containing 20% Nb, the value of $T_c$ increased from 8.2 to 10.5°K with increase of the duration of the 570°C annealing from one to 200 hours.[10] Similar results were obtained for an alloy containing 25% Nb (for example, after 10 hours' annealing at 570°C, $T_c$ increased from 8.7 to 9.6°K). It should be noted that for samples having the largest variation of $T_c$, the superconducting transition, as a rule, was broad: $\Delta T = T_2 - T_1 = 1$°K, where $R(T_2) = 0.9\ R_n$, $R(T_1) = 0.1\ R_n$; whereas for one hour's annealing at low temperatures, $\Delta T \cong 0.02$ to 0.05°K. This is apparently due to the fact that a mixture of phases with strongly differing values of $T_c$ is formed on the contaminated-by-gases surface of the sample during the annealing. Such an explanation is confirmed by the fact that after removal of the most contaminated (and consequently undergoing most complete decomposition) surface layer, the superconducting transition becomes less broad.


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117