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THE CRITICAL CURRENTS OF Nb – Zr ALLOYS IN AN EXTERNAL MAGNETIC FIELD

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The critical currents of specimens from Nb—Zr alloys of various compositions were measured in a transverse magnetic field of up to 23.5 kOe. A marked anisotropy of the critical currents was discovered for cold-rolled tapes. The effect on the superconducting properties of the alloys of deformation and of an anneal subsequent to rolling was studied.

A number of workers[1,2] have shown that Nb – Zr alloys retain superconductivity in fields of ~100 kOe and sustain current densities of $\sim 10^5$ A/cm^2 in fields of up to 30 kOe, and of $\sim 10^4$ A/cm^2 in fields of up to 80 kOe; this, together with the possibility of obtaining cold-rolled tapes and wires from these alloys, makes them very suitable for the construction of superconducting solenoids for fields of 60—80 kOe. An interesting feature revealed by the work of Berlincourt et al[1] is the marked difference (a factor of 2—3) in the critical currents for different orientations of the external magnetic field relative to the plane of rolling of the ribbon-like specimens. Similar observations have been described by Le Blanc and Little[3] for niobium tape.

We have previously[1)] described certain results on the critical currents of tape-like specimens of an Nb + Zr (25%) alloy subjected to various treatments. Measurements of the critical currents of specimens from Nb – Zr alloys of various compositions subjected to various thermal and mechanical treatments are reported in the present article. The data presented, although not complete and final in a number of cases, may be of widespread interest from the point of view both of practical utilization of the phenomenon and of understanding its origin.

We studied a large number of specimens (about 200), mainly fabricated from cold-rolled tapes of Nb – Zr alloys. Specimens of wire, and of tape rolled from wire of small diameter (0.3 – 0.5 mm), were also studied. The study of the variation of the critical current with the angle between the direction of the external field and the plane of rolling of the tape specimens allows additional information to be obtained on the nature of the formations responsible for the extraordinarily high critical values for Nb – Zr alloys. An undoubted advantage of tape specimens also resides in the possibility of increasing the current density in the specimen to $\sim 10^6$ A/cm^2 by making a narrow "neck," while current can be introduced to the specimen in a comparatively simple way.

The critical currents were measured in transverse magnetic fields of up to 23.5 kOe at temperatures of 4.2 and 1.5°K. The specimens from rolled tape of thickness 0.07 – 0.02 mm, length 5 cm and width 3 mm had in their central portions a constriction of cross sectional area 0.01 to 0.12 mm^2. The wire specimens were also 5—6 cm long, and in certain cases a narrower neck was ground in the central portion of the wire. The ends of the specimen were coated with tin for a length of ~1 cm in vacuum at 1000°C. Specimens with electroplated copper ends were also used. The specimens were soldered to the current bus-bars with ordinary soft solder. To prevent heating the specimens when resistance is re-established, a copper wire shunt of diameter 0.8—1.5 mm was soldered in parallel with it. The potential leads were either soldered to the tinned parts of the specimen, or mechanically clamped to its central portion. The critical current was determined for several fixed values of the magnetic field while smoothly increasing the current through the specimen. The re-establishment of resistance was recorded with the aid of a photoelectric galvanometer F-16. The fraction of the current taped off from the specimen by the shunt (which, for a completely superconducting specimen did not usually exceed 5% of the total current) was measured by the same galvanometer and a KL-48 potentiometer.

The electric leads, each in the form of a bundle of three flexible copper strips (of total cross-sectional area 10 mm^2) cooled from above by liquid nitrogen, allowed currents of up to 300 A to

[1)]Paper at the Ninth All-union Conference on Low-temperature Physics, Leningrad, 1962.

be led into the Dewar without particular difficulty. To study the anisotropy of the critical properties the block with the specimens could be rotated by an angle of $\sim 120°$.

RESULTS

A. Cold-worked specimens. The variation of critical current density of cold-rolled specimens with external magnetic field is characterized by the following data. The current density when the field lies in the plane of rolling ($j_{c\parallel}$) diminishes on increasing the field from 0 to 23.5 kOe by a factor of 1.5–2 for specimens containing 12–30% Zr, and by a factor of 3–8 on increasing the concentration of Zr from 40 to 80%. When the field is perpendicular to the plane of rolling, the current density ($j_{c\perp}$) falls by a factor of 20–30 for small concentrations, and of 80–100 for Zr concentrations of 60–80%. The anisotropy of the critical currents $j_{c\parallel}/j_{c\perp}$ then attains a value of 20–30. (These data refer to specimens with 96% deformation.)

The angular variation of j_c for specimens with various degrees of deformation is shown in Fig. 1 for the maximum external field, and the dependence of $j_{c\parallel}$ and $j_{c\perp}$ on the degree of deformation is shown in Fig. 2, where the abscissa axis shows on a logarithmic scale the elongation, which was calculated from the known decrease in tape thickness assuming that there was no transverse broadening during rolling. Curve 1 in Fig. 1, and the points referring to zero deformation in Fig. 2, correspond to a specimen recrystallized at 1400° C after rolling. For cold-rolled specimens in a field of 23.5 kOe, the variations of $j_{c\perp}$ and $j_{c\parallel}$ with Zr content are respectively shown by curves 1 and 2 of Fig. 3. The degree of deformation of all specimens also amounted to 96%.

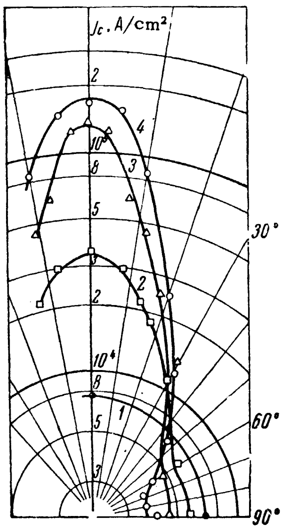

FIG. 1. The dependence of critical current density j_c on the angle between the plane of rolling and the external field (H = 23.5 kOe, T = 4.2°K, alloy Nb + Zr (25%)): 1 – recrystallized specimen, 2 – deformation 80%, 3 – 95.5%, 4 – 97.8%.

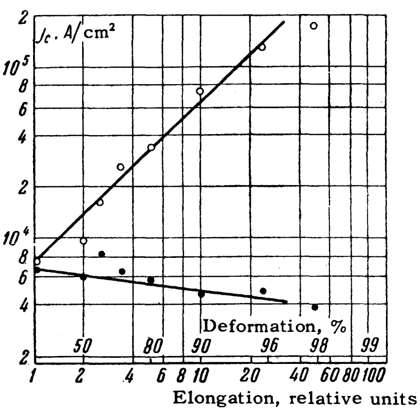

FIG. 2. The dependence of the current densities $j_{c\parallel}$ (o) and $j_{c\perp}$ (•) in a field of 23.5 kOe on the degree of deformation and the magnitude of the elongation (Nb+Zr (25%)).

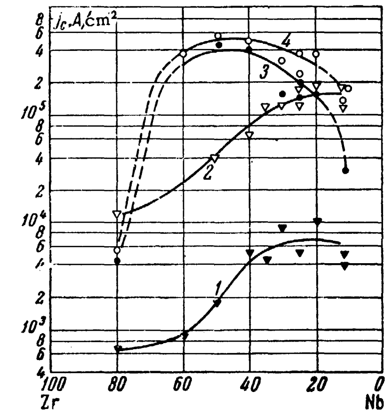

FIG. 3. The values of $j_{c\parallel}$ and $j_{c\perp}$ in a field of 23.5 kOe for cold-deformed specimens and specimens annealed at 600-800°C with various compositions (T = 4.2°K): 1 – $j_{c\perp}$, 2 – $j_{c\parallel}$ (cold-deformed specimens), 3 – $j_{c\perp}$, 4 – $j_{c\parallel}$ (annealed specimens).

The curves in Figs. 1 and 2 show that in the process of deformation by rolling there is formed in the alloys a system of regions superconducting in strong magnetic fields and similar in their properties to a collection of thin plates, the planes of which are parallel to the plane of rolling. The latter assertion follows in particular from the fact that in a specimen cut from rolled tape across the direction of rolling, values were obtained for $j_{c\parallel}$ and $j_{c\perp}$ which agreed well with $j_{c\parallel}$ and $j_{c\perp}$ for the usual specimens, i.e., those cut along the direction of rolling. It is interesting to note that on increasing the deformation the current density $j_{c\perp}$ decreases (Fig. 2). This shows that as the degree of deformation increases, the superconducting regions acquire the properties of more and more perfect "plates."

B. The effect of annealing. In view of the phase transformation observed in the Nb–Zr system[4], we studied in detail the effect on the superconducting properties of the specimens of the time and temperature of an anneal subsequent to cold deformation. The annealing was carried out in high vacuum at temperatures from 500 to 1400°C. Results obtained for one of a series of specimens from a 25% Zr alloy are shown in Fig. 4. The annealing time was three hours in all cases, and the previous deformation of all specimens was 96%. It is noteworthy that the values of j_c for specimens

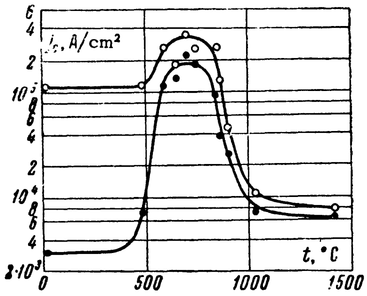

FIG. 4. The variation of $j_{c\parallel}$ and $j_{c\perp}$ in a field of 23.5 kOe with annealing temperature t (alloy Nb + Zr (25%), T = 4.2° K).

annealed in the temperature range 600—850° C increase greatly. When the annealing temperature is further increased the critical current density decreases, and for an annealing temperature of 1000° C reaches values 20—30 times smaller than the maximum.

When the annealing time is increased, the temperature at which the critical current starts to fall (for a three-hour anneal it is approximately 850° C) is displaced to lower temperatures, and, correspondingly, when the annealing time is decreased, this temperature increases. Thus, for example, specimens annealed at 600° C for 100 hours have, in a field of 23.5 kOe, a value of $j_{c\perp}$ of about 2.5 $\times 10^5$ A/cm², and $j_{c\parallel}$ about 4—5 $\times 10^5$ A/cm²; for specimens annealed for 10 hours at 750° C the corresponding values are already 0.65×10^5 A/cm² and 1.1×10^5 A/cm².

Metallographic and x-ray analysis of the specimens shows that in the latter case the phase transformation is already quite far advanced. Thus, on photographs of metallographically polished surfaces taken from these specimens marked changes are noticeable from the "lined" structure usual for rolled tapes; these changes are not observed for shorter times and lower annealing temperatures. Similarly, in Debye photographs of specimens annealed at 750° C for 100 hours, lines of a newly precipitated phase with large Zr content first become clearly discernible. This phase has the same body-centered cubic structure as the original, but with a somewhat large lattice parameter. (The very strongly textured structure of the rolled specimens should be noted; the crystallites are predominantly oriented in such a way that one of the faces of the cube lies in the plane of rolling and its diagonal in the direction of rolling. This preffered orientation is also retained in the phase precipitated after annealing.)

As became known to us subsequently, the increase in the critical current density of wires from Nb—Zr alloys after annealing has been noted (with reference to work still unpublished) by Kunzler,[5] who associated this phenomenon with the effect of stress in the alloy. The occurrence of these stresses in the early stages of the phase transformation is caused, according to generally accepted ideas, by the separation from a homogeneous solid solution of two phases of different composition with somewhat differing specific volumes. In the subsequent stages of decomposition the dimensions of the precipitated formations increase (phase coagulation), which should diminish the stresses. This stage corresponds, apparently, to the decrease of critical current density after annealing at higher temperatures and longer times. The fact that the temperature at which a worsening of the critical properties is observed does not coincide with the temperature at which decomposition starts, but lies below the latter, thus finds a satisfactory explanation.

It is, however, possible that the role of decomposition in the mechanism which provides the increase of critical current is not limited to one of increasing the stresses. The growth of concentration inhomogeneities, and the separation of the phase by microscopic distances comparable with the penetration depth during the initial stages of the decomposition can, it seems, create in the alloy a microscopic "sponge-like" structure, approximating in its superconducting properties to a system of fine threads possessing exceptionally high critical parameters. To establish the actual nature of the mechanism referred to, of particular value are studies of the critical fields (for small measuring currents), the values of which should be very sensitive to the dimensions of inhomogeneities in the alloy.

We also started measurements of the critical currents of annealed specimens previously subjected to various magnitudes of deformation, and of specimens of various compositions. The first results show that the rate of the processes which change the critical current during annealing decreases when the previous deformation is decreased. The increase of this rate when the deformation is increased apparently causes the diminution of critical current density to start at lower annealing temperatures. At the present time the effect of previous deformation on the optimum current density is being investigated (by the optimum current density we mean that attained under most favorable annealing conditions).

The results of some measurements of the critical currents of annealed specimens of various compositions are shown in Fig. 3 (curves 3 and 4). The increase of critical current density after annealing at 600—700° C was observed in all Nb—Zr alloys for which a phase transition should be observed. It is seen that alloys containing 60—40% Zr give, after annealing, somewhat larger values of j_c than alloys containing 30—20% Zr (for equivalent previous deformation). This observation agrees with the remark contained in Kunzler's review,[5] where the easier workability of 60—40% Zr alloys is also mentioned. These alloys appear to be a basic material for making solenoids for 70—80 kOe fields.

The annealing of specimens from an alloy with 12% Zr, for which no phase transition should occur, produces no essential increase of $j_{c\parallel}$, but $j_{c\perp}$ increases to $\sim 0.4 \times 10^5$ A/cm^2 for a specimen annealed at 800° C for three hours. It is possible that this quite significant increase of $j_{c\perp}$ is related to inadequate homogeneity of the specimens studied. Zirconium-rich inclusions decomposing at 600—850° C could cause $j_{c\perp}$ to increase after annealing. An analogous situation apparently also occurs with 80% Zr composition. With the aim of studying the change of properties of annealed specimens when one moves from concentrations for which decomposition occurs below 900—600° C to concentrations stable at all temperatures, measurements are currently being made on the critical currents of specimens with various annealing temperatures and zirconium concentrations ranging from 5 to 20%.

We are extending the measurements described into the region of very high fields (60—70 kOe), where the longitudinal field case is also being studied. Studies have also been started on the possible changes of critical temperature due to annealing in alloys of various composition.

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