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High-Field Superconductivity in Some bcc Ti-Mo and Nb-Zr Alloys*

Abstract: Zero electrical resistance at unusually high magnetic field strengths has been observed in the bcc alloys Ti-16 a/o (atomic percent) Mo, Nb-12 a/o Zr, and Nb-25 a/o Zr. The maximum high-field zero-resistance current density, J_c, in these alloys appears to be a sensitive function of temperature, the degree of cold-working, and the orientation of the applied *transverse* magnetic field. For cold-rolled alloy specimens in an applied transverse field, J_c is a maximum or minimum, according to whether the field is set respectively parallel or perpendicular to the rolled face of the specimen. In Ti-16 a/o Mo the zero-resistance condition is observed in fields at least a factor 35 greater than the bulk material critical field as inferred from calorimetric data.

Introduction

Zero electrical resistance at unusually high magnetic fields has been observed in the transition-metal alloys Ti-16 a/o (atomic percent) Mo[1] and Mo-25 a/o Re,[2] and in the compound Nb_3Sn.[3-5] The high-field zero-resistance behavior in these materials appears to be an extreme example of the well-known separation of resistive and magnetic superconducting transitions in "hard" superconductors.[6] Such behavior, as well as the attendant flux-trapping, is commonly attributed to the existence of a "sponge" of fine filaments with high critical fields situated within relatively low critical-field bulk material. Since the high-field filaments are variously thought to be associated with highly strained regions, dislocations, impurities, inhomogeneities, et cetera, it is natural to look for further extreme examples of "hard" superconductivity in various cold-worked transition metal alloys, where a high degree of lattice imperfection and strain is to be expected. The present results were obtained during the course of a systematic investigation of resistive superconducting transitions in various Ti, Zr, Nb, Hf, and Ta-rich alloys in magnetic fields up to 30 kgauss, and have been chosen as illustrative of the high-field superconducting behavior so far encountered.

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Ti-Mo specimens

Figure 1 shows curves of critical current density, J_c, vs *transverse* magnetic field strength, H, for Ti-16 a/o Mo specimens in the cold-rolled (K_R) and unrolled (K_U) conditions. K_R was cold-rolled from a thickness of ≈ 0.11 cm to a thickness of 0.023 cm. The cold-rolled strip was then sheared to a width of 0.11 cm and a length of ≈ 2.5 cm. Specimen K_U is the same specimen, K, measured previously in work on the normal state resistivities, the Hall coefficients, and the resistive superconducting transitions of bcc Ti-Mo alloys.[1] This specimen was sawed and ground to shape ($\approx 2.5 \times 0.3 \times 0.025$ cm) without cold rolling. Transition temperature (T_c) measurements in the Ti-Mo system via a magnetic susceptibility technique indicate a T_c for Ti-16 a/o Mo of about 3.7°K,[7] in fair agreement with a resistive measurement of T_c for specimen K_U at 48 amp/sq cm.[1] At the same current density, specimen K_R showed zero-resistance at 4.2°K, indicating that cold rolling had elevated the resistive superconducting transition temperature. The J_c vs H data of Fig. 1 were taken by slowly increasing the current through the sample at constant field strength until the least detectable voltage (≈ 0.25 μv) was observed. The current required to produce this voltage divided by the cross-sectional area of the specimen was defined to be the "critical current density", J_c. The specimens were copper-plated over ≈ 0.6 cm at their ends and were then soft-soldered between copper current lugs. The copper potential leads (spaced about 0.7 cm apart) were clamped against the specimens with beryllium-copper spring clips.

For the cold-rolled specimen, K_R, the J_c vs H curves of Fig. 1 show that J_c values are markedly dependent upon the direction of the transverse magnetic field *relative to the rolled face of the specimen.* Polar plots of J_c vs transverse field orientation are roughly elliptical in shape with maxima and minima at field directions respectively parallel ($H\|$) and perpendicular ($H\perp$) to the rolled faces of the specimen. The ratio J_c (30 kgauss, $H\|$)/J_c (30 kgauss, $H\perp$) in specimen K_R is 31 at 2.4°K and 23 at 1.2°K. The field orientation dependence observed here, in fields where flux penetration of the specimen is doubtless nearly complete, is not to be confused with the well-known orientation dependence of the bulk specimen superconducting transition, which is determined strictly by the specimen geometry (the demagnetizing coefficients). J_c vs H curves measured for a Ti-16 a/o Mo specimen, cold-rolled to an identical thickness with identical reduction but three times the width of K_R, were nearly the same as those for K_R shown in Fig. 1. A less prominent transverse field orientation dependence is observed for the unrolled specimen, K_U. In this case the maximum and minimum values of J_c are observed with the magnetic field set respectively parallel and perpendicular to the wider (0.3 cm) ground face of the specimen.

Figure 1 **Critical current density, J_c, for restoration of the first observable resistance vs applied *transverse* magnetic field, H, for Ti-16 a/o Mo alloy specimens K_U and K_R at different temperatures and field orientations.** *K_U is an unrolled specimen which was ground to shape and for which the $H\|$ and $H\perp$ designate H respectively parallel and perpendicular to the wider ground face of the specimen. K_R is a cold-rolled specimen for which $H\|$ and $H\perp$ designate H respectively parallel and perpendicular to the rolled face of the specimen.*

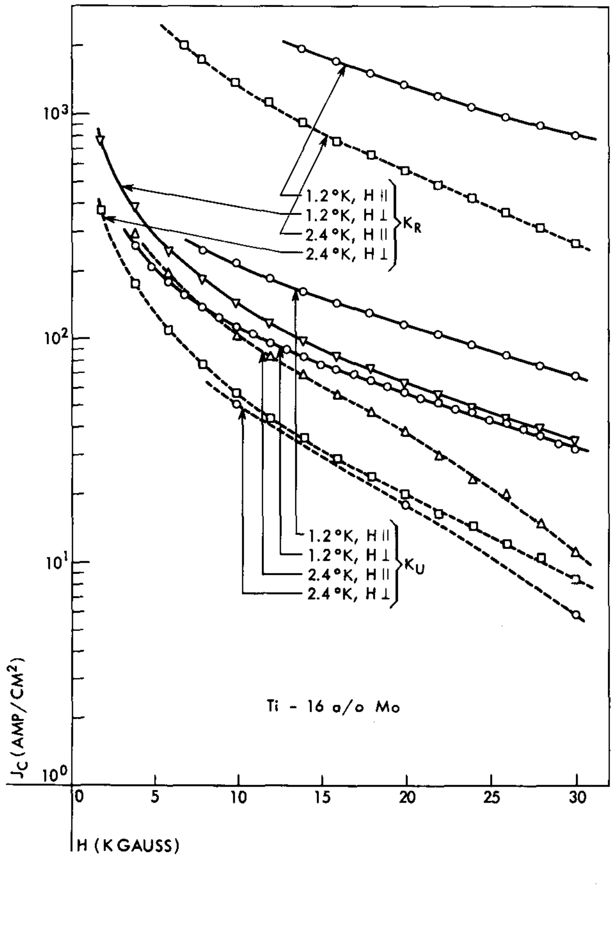

Figure 1 also shows that cold rolling increases the J_c (30 kgauss, $H\|$) value by a factor of 12 at 1.2°K, and a factor of 24 at 2.4°K, but does not appreciably alter the J_c (30 kgauss, $H\perp$) values. J_c values are also very sensitive to temperature, the greatest sensitivity being observed in the unrolled specimen, K_U, where J_c (30 kgauss, $H\|$, 1.2°K)/J_c (30 kgauss, $H\|$, 2.4°K) = 6.

Although the bulk specimen critical fields, H_c, have not been measured for Ti-Mo alloys, a crude estimate of $H_c(T = 0°K) \equiv H_0$ is possible. The electronic specific heat coefficient, γ, for bcc Ti-Mo alloys has been measured as a function of Mo concentration between 6.25 and 8.60 a/o Mo.[8,9] If these measured γ values are extrapolated linearly to the 16 a/o Mo concentration, a value $\gamma = 9 \times 10^{-3}$ joules/mole $(°K)^2$ is obtained. This figure is doubtless an upper limit, since the Mo concentration dependence of the T_c values[7] suggests that γ drops below the linear extrapolation above about 10 a/o Mo. Using the well-known relationship between γ and $(H_0/T_c)^2$ (as given, for example, by Bardeen, Cooper, and Schrieffer[10]), $T_c = 3.7°K$, and a molar volume $V_m = 10$ cm, we[3] obtain $H_0 = 860$ gauss, probably constituting an upper limit. Hence for Ti-16 a/o Mo it appears that superconductivity exists in magnetic fields (30 kgauss) at least a factor of 35 greater than the bulk material critical field.

The high-field superconducting behavior of Ti-16 a/o Mo may be explicable in terms of a negative free-energy at super-normal interfaces arising because the short electronic mean free paths (hence superconducting "coherence distances") in this high resistivity alloy (105 μohm-cm just above T_c[1]) are comparable with the penetration depths.[11] The 12–24-fold increase in J_c ($H\|$) values due to cold rolling is not, however, accompanied by a large change in the 4.2°K normal state resistivity (the change appears to be less than 12%). The large transverse field orientation dependence of the J_c values could be associated with preferred crystalline orientation and/or the configuration of the dislocation network.

Nb-Zr specimens

More notable high-field superconducting behavior has been observed in cold-worked bcc Nb-Zr alloys[12,13] which have T_c values around 11°K.[14] J_c values as high as 10^5 amp/cm^2 at 30 kgauss and 4.2°K have been measured in cold-drawn Nb-25 a/o Zr wires of 0.015 cm diam and in 0.025 cm diam wires which have been cold rolled to a thickness of 0.007 cm. For specimens fabricated in the latter fashion, preliminary pulsed-field measurements indicate a J_c value of 2×10^4 amp/cm^2 at 80 kgauss and 1.2°K. Critical currents have been found to *increase* with increase of the externally applied field in some cold-rolled Nb-12 a/o Zr alloys,[15] giving rise to a pronounced peak in the J_c vs H curves at about 25 kgauss. In such cases the zero-resistance condition can actually be destroyed by the reduction of the externally applied magnetic field. The transverse field orientation dependence of J_c for cold-rolled specimens of Nb-Zr is similar but less pronounced than that observed in Ti-16 a/o Mo. The ratio J_c (30 kgauss, $H\|$, 4.2°K)/J_c (30 kgauss, $H\perp$, 4.2°K) has varied between 2 and 3 for cold-rolled Nb-12 a/o Zr and Nb-25 a/o Zr specimens. As in the case of Ti-16 a/o Mo specimens, a very wide range of J_c (30 kgauss) values is observed for Nb-Zr specimens of the same nominal alloy composition. Further investigation will be required to isolate the important variables affecting the high-field superconducting characteristics.

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Note added in proof

A maximum zero-resistance current density of 1.6×10^5 amp/cm^2 at 4.2°K and 30 kgauss has been observed in a sample obtained by cold rolling a 0.036 cm diam Nb-25 a/o Zr wire to a thickness of 0.010 cm, and then filing to a width of 0.013 cm. A superconducting solenoid has recently been constructed using 0.010 in. diam Nb-25 a/o Zr wire which is now available commercially (from the Wah Chang Corporation of Albany, Oregon). The solenoid has a length of 5 cm, an i.d. of 0.5 cm, an o.d. of 6.8 cm, and generates a peak field of 60 kgauss at a current of 17.2 amp (a current density of 34,000 amp/cm^2 in the superconducting wire). For details of an earlier magnet of the same type see R. R. Hake, T. G. Berlincourt, and D. H. Leslie, *Proceedings of the 1961 International Conference on High Magnetic Fields*, John Wiley and Sons, Inc., New York, to be published.

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