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SIZE EFFECTS AND INTERSTITIAL IMPURITIES

IN Nb_3Zr SUPERCONDUCTORS.

SUPERCONDUCTING SOLENOIDS WITH

METAL INSULATION

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OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

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ABSTRACT

Small additions of oxygen and carbon were found to increase the critical currents of Nb₃Zr wires in the precipitated condition. Interstitial elements are thus associated with the precipitation enhancement of critical currents and with the variation in the critical currents of different lots of Nb₃Zr. Wires of Nb₃Zr were prepared in various diameters by cold drawing, etching, and grinding. Each wire was made so that the cold working was the same at each final size. Under these circumstances, critical currents were nearly proportional to wire diameters, and strong increases in the critical-current densities occur with smaller sizes, particularly in wires thinned by etching. The critical-current density of an 0.0009-in. wire was 3.3×10^5 amp/cm² at 25,000 gauss. A second series of experiments varied the amount of cold working while keeping the final wire diameter constant. The cold working of precipitated Nb₃Zr wire beyond 90% decreases critical-current density slightly. The results are discussed in terms of filamentary current models with the conclusion that most of the current is near the surface of the wire.

Superconducting magnets can be severely damaged by fast transitions from the superconducting to normal states. In many cases, the critical currents in coils have been smaller than in short sample tests. Two superconducting Nb₃Zr solenoids were built with pure metal foils between layers and with alloy or no insulation between turns. The transition times range between 6 and 30 sec at peak fields, 22 to 31 kilogauss, to 10 to 15 msec at 10 to 15 kilogauss. These times are long enough to provide reasonable lifetimes of small coils. One coil has been in almost daily use for five months without a decrease in critical current. The

second coil was wound with Nb₃Zr wire which had been precipitated at 800°C. The critical coil currents (8×10^4 amp/cm² at 22,000 gauss) agreed excellently with short-wire tests of the same wire.

INTRODUCTION

Superconducting coils of niobium-zirconium were shown earlier¹⁻⁵ to have smaller critical current densities than short samples tested in an external field. Although there are many factors which could lead to reduced critical coil currents, such as poor joints, wire loosened by thermal contraction, and weak points in the wire, the effects for the present discussion will be assumed to be due to conditioning.^{1,6-9} Conditioning occurs where a sample is cooled from above the transition temperature into a steady field, and the critical current is then measured by repeatedly transforming the wire into the normal state. The critical currents gradually increase from low initial value to a final higher and limiting value. Similar effects are observed after the external field is changed to a new value without changing the sample temperature. In some cases, the conditioning effect has been shown to be due to changes in the joints or mechanical motions in the sample during testing. However, even with good joints and mechanically secure samples, conditioning effects still exist. This type of conditioning effect is believed to be

¹S. H. Autler, Proceedings of the International Conference on High Magnetic Fields, Cambridge, 1961 (Massachusetts Institute of Technology press and John Wiley and Sons, Inc., New York, 1962), pp 324-31.

²J. K. Hulm, M. J. Fraser, H. Riemersma, A. J. Venturino, and R. A. Wien, Ibid., pp 332-40.

³R. R. Hake, T. G. Berlincourt, and D. H. Leslie, Ibid., pp 341-43.

⁴J. E. Kunzler, Ibid., pp 574-79.

⁵J. O. Betterton, Jr. and D. S. Easton, Ibid., pp 348-57.

⁶G. D. Kneip, Jr., R. E. Worsham, J. O. Betterton, Jr., R. W. Boom, and C. E. Roos, "Hysteresis Effects in the Nb₃Sn Superconducting Transition," paper presented at the American Physical Society Meeting, Washington, D. C., April 24-27, 1961.

⁷M. A. R. LeBlanc, Phys. Rev. **124**, 1423 (1961).

⁸P. Aron and H. C. Hitchcock, Superconductivity of Nb-25 at. % Zr Alloy in High dc Magnetic Fields (University of California, Lawrence Radiation Laboratory, Berkeley, California), UCRL-9790 (July 18, 1961).

⁹P. Aron and H. C. Hitchcock, Anomalous Critical Currents in Nb-25 at. % Zr Wire (University of California, Lawrence Radiation Laboratory, Berkeley, California), UCRL-10087 (February 16, 1962).

due to trapped flux^{6,9} or to motion of dislocation filaments during slight heat pulses of the tests. Earlier short samples of precipitated Nb₃Zr (ref 10) were free from most of this conditioning. If the strains introduced by precipitation eliminate the conditioning phenomenon, straight-wire and coil tests will agree. A solenoid made from wire of this type will be described below in order to test this idea.

A superconducting coil with conventional insulation of inductance L and with a low resistance shunt r has a time constant L/r . The normal-state resistivity of Nb₃Zr is $17.7 \mu\text{ohm}\cdot\text{cm}$ near 4.2°K . The transition to the normal state of any reasonable fraction of the coil will result in a large coil resistance and rapid dissipation of the magnetic field energy $1/2 Li^2$. Assuming that the superconducting current is carried in filaments, the energy will be dissipated at the breaks in these filaments. Local temperature increases sufficient to disorder the filament dislocation structure then may result from the low specific heat of the wire. Experimental superconducting coils with conventional insulation on an iron-core magnet showed steady decreases in critical coil current after a number of days of operation.⁵ These effects were thought to be due to a process similar to that described above.

In order to further investigate the critical currents and the normal-state damage, new coils were prepared with more complete shunting by pure metal foils and with wire which had been given an isothermal 800°C precipitation heat treatment.¹⁰ The object was to see if increased time constants could be obtained during the transition to the normal state and to see if wire which consistently showed very little training effects in short-wire tests would have improved current density in the coil form.

THE IRON-CORE MAGNET

Following a recent coil design by Hake, Berlincourt, and Leslie,³ bare 0.010-in. Nb₃Zr wire was wound on coil forms for an experimental Hiperc magnet and 0.003-in. soft aluminum foil was placed between each

¹⁰G. D. Kneip, Jr., J. O. Betterton, Jr., D. S. Easton, and J. O. Scarbrough, Proceedings of the International Conference on High Magnetic Fields, Cambridge, 1961 (Massachusetts Institute of Technology press and John Wiley and Sons, Inc., New York, 1962) pp 603-8.

layer. The experimental arrangement of the magnet is shown elsewhere.⁵ The new coil forms each contained approximately half of the turns of an inner section of 1252 turns and an outer section of 817 turns. The fields produced in the 4.1-cm x 1.2-cm x 0.3-cm gap of the magnet at 4.2°K are shown in Fig. 1 as a function of the coil current for each section and for the sections in series. As in earlier work with this magnet, the critical current of the coils depends upon the number of turns and is limited by the amount of flux escaping from the Hiperco core. The present coils wound with bare wire are of particular advantage for conserving space in small solenoids. The absence of even a slight resistance in the spot-welded joints in the final assembly is indicated by good reproducibility of the field vs current curves, by stability of persistent currents, and by the helium consumption of 200 cm³/hr during persistent current operation at 30,000 gauss. Hysteresis was smaller than the 1/2% experimental error in the field measurement and was ± 70 gauss at zero current. Fields were measured with a flip coil, calibrated at helium temperatures with Li⁷ nuclear resonance.

The time constants of the magnet were increased compared to the earlier Formvar insulated coils on the same Hiperco core. With the coils in the superconducting state, the rise times and decay times were of the order of 2 to 3 min. The transition to the normal state was slow, with a relaxation time of the order of 12 sec when the field was in the range 10 to 15 kilogauss. At higher fields and with the current in the coils closer to the critical values, the transition occurred more rapidly as shown by the oscilloscope traces of Figs. 2 and 3. Figure 2 shows a characteristic trace of the voltage induced in the idle 817 turn superconducting coil during the decay of a 28,000 gauss field. The field had been generated by superconducting current in the 1252 turn coil. The photographs were taken by rapidly switching off the applied voltage on the magnet which at higher fields induced a transition. The time for the transition to minimum field was approximately 240 msec. This time and the other times obtained from the oscilloscope traces for these coils refer to the total time interval for the induced voltage to return to zero. An exponential time constant was not observed because of an

Fig. 1. Field Strength vs Current of the Hiperco-Core Magnet.

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Fig. 2. Transition Time of 1252 Turn Al-Foil Coil From 28 Kilogauss. Vertical scale: Induced voltage in idle 817 turn coil, 50 mv/cm. Horizontal scale: 0.2 sec/cm. Time: 240 msec.

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Fig. 3. Transition Time of 1252 Turn Al-Foil Coil From 24 Kilogauss. Vertical scale: Induced voltage of idle 817 turn coil, 1 mv/cm. Horizontal scale: 0.5 sec/cm. Time: 1.5 sec.

unusual increase in the field and a positive induced voltage in the later stage of the field decay. Figure 3 shows that at 24,000 gauss with the same 1252 turn coil the transition time to minimum field is 1.5 sec. Other tests at 30 to 31 kilogauss show transition times in the range 30 to 50 msec. The times interval appears to be related to the number of turns in the coil which transform to the normal state. The transition takes place more fully in the higher field case where the magnetic field energy is highest. The increase in transition times has improved the lifetime of the present coils. The present coils have been in almost daily use for five months without any decrease of their critical currents.

The critical currents of short lengths of the same 0.010-in. Nb₃Zr wire are larger than in the Hiperco coils, as shown in Fig. 4. At the maximum fields which would be expected near the coils, the coil-current densities are only one quarter or one third of the short-wire values. The coil currents are shown by the vertical bars at 6 kilogauss where they may be compared to short pieces of the same wire in the curves above. It is of interest that short samples from different coils of Wah Chang wire agreed with each other.

INCONEL INSULATED AIR-CORE SOLENOID

In order to investigate coil-current densities further, a small air-core solenoid was made from 0.006-in. Inconel insulated wire which had been fabricated at the Oak Ridge National Laboratory (ORNL) with an isothermal anneal at 800°C during fabrication. This wire had shown very little of the training effects in short-wire tests. The solenoid was wound as shown in Fig. 5 with copper foil between layers and without other insulation. Experimental fields attained with each section and with both sections in series are shown by the table at the bottom of Fig. 5. The values compare favorably with fields computed by the Fabry method as modified by Boom and Gauster.^{11,12} The time constants in the

¹¹R. W. Boom and R. S. Livingston, "Superconducting Solenoids," paper presented at the Wescon Conference, Los Angeles, California, July 15, 1961. (To be published in IRE Proceedings.)

¹²W. Gauster, Trans. Am. Inst. Elec. Engrs. 1(51), 822-8 (1961).

Fig. 4. Comparison of Critical-Current Densities of the Wire and the Coils of the Hiperco Magnet.

Section	Turns	H_{0z} (gauss/amp)	H_{ca1c}^* (gauss/amp)	H_{obs} (gauss/amp)	H_{a1} (gauss/amp)	i_c (amp)	H_{a1} (gauss)	i_c (amp/cm ²)
1	1080	583	592	590	604	19.8	11,950	1.08×10^5
2	1848	823	855	855	915	17.5	16,000	0.955
1 + 2	2928	1412	1442	1445	1472	15.1	22,200	0.825

*Av over area of search coil.

Fig. 5. Inconel Insulated Superconducting Solenoid.

superconducting state for this coil were of the order of 1 to 2 min. In order to keep the field constant for experimental purposes, this magnet has been operated with persistent currents. A Nb₃Zr shunt was wound over a small graphite resistor and connected to the solenoid leads in the helium Dewar by spot-welded joints. Constant fields were maintained for four hours to within the 0.5% accuracy of our measuring devices. The persistent mode of operation is convenient with a long-time constant since the field could be stabilized without waiting for equilibrium to be attained. The thermal switch was a useful way to quench the magnet from several different fields, and the oscilloscope traces shown in Figs. 6 and 7 were obtained in this way.

Figure 6 shows the induced voltage in a 300-turn search coil in the center of the solenoid when the coil was quenched from 21,000 gauss. The photograph did not record the first negative portion of the trace as the beam speed was high in this region. The induced voltage became positive in the later part of the transition in the same manner as with the Hiperco magnet. The time to minimum field from 21,000 gauss was 6 msec. Then as shown in Fig. 7, at 12,500 gauss the transition time to minimum field was found to be 20 msec and for fields below this, only slow transitions could be attained. There has been no indication of change in the critical-current density with the use of this solenoid.

The most important result which was observed in the Inconel insulated solenoid was the relatively good agreement between the short-wire tests and the solenoid critical-current densities. This is shown in Fig. 8 where the critical currents of the coil operated in various sections are plotted against short-wire tests from the same material. Current densities of 8.2×10^4 amp/cm² were observed with a 22-kilogauss field at the inner turns of wire. Since conditioning effects were not observed in the short-wire tests, it may be that the agreement between the coil and wire currents is due to a more effective pinning of dislocations by the isothermal 800°C heat treatment. This is not the only interpretation, however, as the Inconel insulation may effectively prevent induced currents in adjacent turns caused by shifting of the current paths in the individual wires as the current is increased. An

Fig. 6. Six Milliseconds Transition to Normal State. Inconel insulated coil at 21 kilogauss. Horizontal scale: 2 m/sec-cm (self-triggered at -3 cm). Vertical scale: 100 mv/cm (zero at +2 cm).

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Fig. 7. Twenty Milliseconds Transition to Normal State. Inconel insulated coil at 12.5 kilogauss. Horizontal scale: 5 m/sec-cm (self-triggered at -3 cm). Vertical scale: 100 mv/cm (zero at +2 cm).

Fig. 8. Comparison of Critical-Current Densities of Short-Wire Tests and of the Inconel Insulated Solenoid.

effect such as this could cause the anomalous voltages observed across short samples.^{6,8} Furthermore, great care was taken in winding the coil and the space factor for the finished coil was very nearly that for ideal packing so that the improved result may be due to a stiffening effect of the Inconel jacket and to firm positioning of the turns between the copper foil layers. No matter which interpretation is taken, an agreement of coil and short-wire critical-current densities has been obtained in the medium field region.

EFFECTS OF INTERSTITIAL IMPURITIES ON THE CRITICAL CURRENTS OF NIOBIUM-ZIRCONIUM ALLOYS

It is known in refractory metal studies¹³⁻¹⁵ that alloying with a more electropositive solute in the presence of the normal interstitial impurities in these refractory metals will produce strong effects in the mechanical properties and microstructure of these metals. In order to investigate the precipitation process which improves the current density of niobium-zirconium¹⁰ from this point of view, alloys were prepared with additions of 100 and 250 ppm O₂ and with 200 ppm C.

Alloys were prepared from single Nb₃Zr casting which was divided into four parts. Additions of 100 ppm O₂, 250 ppm O₂, and 200 ppm C were made to three portions by arc casting the Nb₃Zr with the compounds ZrO₂ and ZrC. The alloys were cold swaged to 0.15 to 0.20 in. and analyses were determined as shown in Table 1. The results agreed with the synthetic additions with the exception of the 250 ppm O₂ alloy. The results for this alloy were considerably higher in hydrogen and oxygen than expected. The analysis sample in this case was the end of the swaged ingot which was so badly cracked that the cracks could not be ground away. The higher results are believed to be due to entrapment of gases and etching residues in these cracks. Attempts were made to analyze small-diameter wires prepared from these ingots. The

¹³J. W. Martin, J. Less Common Metals 2, 392 (1960).

¹⁴D. O. Hobson, "Aging Phenomena in Columbium-Base Alloys," paper presented at the AIME High-Temperature Materials Conference, Cleveland, Ohio, April 26-27, 1961. Also ORNL-3245 (March 16, 1962).

¹⁵Warren I. Pollock, "Recent Developments in Columbium Physical Metallurgy," paper presented at the Golden Gate ASM Conference, San Francisco, 1961.

Table 1. Analyses of the Nb₃Zr Superconductors
Used in the Wire Tests

Specimen Identifi- cation	O ₂ ^a (ppm)	N ₂ ^a (ppm)	H ₂ ^a (ppm)	C ^b (ppm)
No addition	56	17	5	80
200 ppm C	91	25	10	280
100 ppm O ₂	170	21	7	-
	160	18	6	-
250 ppm O ₂	470 ^c	20	160 ^c	-
	520 ^c	24	150 ^c	-

^aPlatinum-bath vacuum-fusion method.

^bLeco-combustion method.

^cQuestionable values determined with badly cracked surfaces.

results showed differences due to the synthetic additions but always with higher oxygen content (200 to 300 ppm additional) and higher hydrogen content (90 to 130 ppm additional). The values were suggestive of considerable surface contribution to the analysis. Since the wires were prepared by room-temperature deformation, these high results for fine wires and for the cracked 250 ppm alloy are not considered to be typical of the interior of wires, but more representative of physically attached impurities. In support of the above, microscopical study of the fractures of cold drawn Nb₃Zr wires show loose fibrous nature in these wires and a rough surface. Analysis of such materials in large coherent pieces would lead to more realistic results. For the present discussion, the values given on the first four lines of Table 1 are considered to be representative of the alloy composition. For the 250 ppm alloy, the synthetic addition will be assumed making the oxygen content about 300 to 350 ppm.

The alloys were fabricated to 0.016-in. wire, according to the schedule given in Fig. 9. Critical-current densities were measured in a transverse field provided by the Hiperco-core superconducting magnet. The normal state was detected by the current transfer to a low

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Fig. 9. The Effect of Adding Interstitial Elements.

resistance shunt. Earlier experiments have shown that this current transfer corresponds closely to the development of a 10^{-6} voltage across the specimen. Specimens were securely taped with Mylar to a sturdy support so that the center 4 cm of the 9-cm specimen was in the uniform field of the electromagnet. The indium-soldered joints at the end of the specimen were in fields of the order of 10% of the value plotted. There was a notable absence of conditioning effects in the specimens. In the 4 to 6 determinations of critical-current density which were made at each field point, the current reproducibility was within 3%. Larger errors occasionally occurred when the currents were unusually large, as in top curve of Fig. 9, or when errors occurred from other sources such as diameter measurement or fabrication variables. All measurements to be described in this paper were made in liquid helium at 4.2°K. The amount of cold working will refer to the percentage reduction in area from the preceding anneal. The amount of cold work between the homogenization and the intermediate precipitation anneal was kept constant for all of the specimens.

The effects of oxygen and carbon on the critical-current densities of Nb₃Zr wire of diameter 0.016 in. are shown on Fig. 9. The alloys with added oxygen and carbon have considerably increased critical-current densities. Since the alloys had been heat treated for 15 min at 800°C during the fabrication, the improved properties were thought to be related to more effective precipitation in the presence of these elements. This was investigated in the case of the 250 ppm O₂ addition by preparing wires with and without the 800°C anneal, as shown in Fig. 10 for 16-mil-diam wire. In the lower curves of this figure, the critical-current densities of nonprecipitated Nb₃Zr are the same with and without the 250 ppm O₂ addition. On the other hand, the 250 ppm O₂ addition makes a remarkable difference in the increase in critical currents due to the 800°C heat treatment, as shown by the upper curves. It should be explained with Fig. 10 that little recrystallization occurs in Nb₃Zr in 15 min at 800°C on the basis of x-ray photographs. The intermediate precipitation heat treatment, therefore, did not essentially change the amount of cold working in the wires of Fig. 10.

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Fig. 10. Effects of Oxygen on the Change in Critical-Current Density with 800°C Heat Treatment.

Similar effects were observed at wire diameters 0.005 in. with greater amounts of cold working as shown in Fig. 11. The oxygen effect in this case was to reduce the critical-current density in the absence of 800°C heat treatment and to increase the critical-current density with the 800°C heat treatment. With this increased amount of cold working, no effect of 800°C heat treatment was detectable in the lower oxygen control sample.

The results would indicate that oxygen is associated with the precipitation which increases the critical currents in Nb-Zr alloys. The increase in the critical currents is apparently not due to the interstitial solid solution of oxygen. The exact form of the precipitation is still not established. One suggestion is that a metastable coherent precipitate ZrO forms during the 800°C heat treatment. This precipitate with a cubic, rock salt-type structure was found by extraction replica and electron-diffraction techniques by McNutt¹⁶ in Nb-10% Zr after precipitation at 1200°C. McNutt has concluded that this substance is a transition phase which with longer aging will eventually form ZrO₂. Hobson¹⁴ has observed ZrO₂ diffraction lines in Nb + 1% Zr containing at least 1400 ppm O₂ which was heat treated at 1600°C. Hobson has also proposed that aging this alloy at 800 to 900°C after solution heat treatment at 1600°C produces either ZrO₂ or a coherent metastable transition phase which ends up as ZrO₂. Debye-Scherrer x-ray photographs of the present cold-worked Nb₃Zr did not show evidence of additional lines or other changes due to addition of 250 ppm O₂. The patterns were diffuse and the method would be expected to be insensitive to precipitate. The beneficial effect of carbon in Nb₃Zr would indicate that this element is also associated with the precipitation which increases the critical currents in Nb-Zr alloys. Pollock¹⁵ has suggested that the rock-salt compounds ZrC or ZrC-NbC are important in precipitation reactions in alloys of this type. The elements, oxygen, carbon, and

¹⁶J. E. McNutt and G. D. Gemmell, "Precipitation Hardening in Columbium Alloys," paper presented at AIME Fall Meeting, Detroit, October, 1961.

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Fig. 11. Effects of Oxygen on the Change in Critical-Current Density with 800°C Heat Treatment.

including nitrogen and hydrogen, can be expected to damage the workability and to improve the critical currents at different rates. Future Nb₃Zr superconductors can undoubtedly be improved in both workability and critical currents by controlled adjustment of these elements.

SIZE EFFECTS AND COLD WORKING IN NIOBIUM-ZIRCONIUM

A size-effect study in niobium-zirconium superconductors was made to provide information about the distribution of the superconducting currents in cold-worked and precipitated material. In order to investigate the dependence on fabrication procedures, wires were made in several different ways. Two sets of specimens were made by normal techniques, one at constant wire diameter with different amounts of cold working and the other at a constant amount of cold reduction with different wire diameters. To accomplish this, an ingot was swaged to the appropriate diameters; the samples were homogenized in a single quartz capsule for 1 hr at 1500°C, cold swaged 48%, and then precipitated for 1 hr at 800°C. The precipitation was done in a single capsule and in a series of gauges. Finally, the wires were drawn to the appropriate diameters. In addition, sets of specimens of constant cold work but varying diameters were obtained by etching wires from 16, 10, and 5 mil starting gauges and by grinding wires with emery paper from 13 and 10 mil diameters. For the etched and ground wires, the cross-sectional area of the wires were frequently elliptical in shape and the transition from the superconducting to normal state was assumed to first take place where the current density was highest, i.e., at the point of minimum area. This minimum area was chosen by rotating the wires in an optical comparator and measuring the major and minor diameters of several minimum areas along the wire axis. No significant changes in the current densities were observed for the two etching reagents, 75 HNO₃-25 HF and 50 HNO₃-10 HF-10 H₂SO₄.

The effect of cold working is shown in Fig. 12 for wires of two sizes. The critical-current density at two field strengths is plotted against the logarithm of the ratio between the initial and final cross-sectional areas of the wires. The effect of cold working was quite small; and, in the range 98 to 99.9% reduction in area, the critical-current

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Nb₃Zr 1 hr 1500°C + 48% CW + 1 hr 800°C + VARIOUS CW

- 5-mil DIA
- 10-mil DIA

Fig. 12. Changes in Critical-Current Density with Cold Work.

densities decreased slightly with increased amounts of cold work. This decrease is believed to be due to a disordering of the strains arising from the precipitation heat treatment which preceded the cold working. It could also be due to special conditions where dislocations are reduced in density with further cold work. The results suggest that in heat-treated Nb_3Zr higher critical currents would be obtained by cold reduction to smaller amounts than normally employed. Nonheat-treated Nb_3Zr would be expected to have a normal cold working effect and care should be taken not to extend these results to other hard superconductors where conditions may be entirely different.

The effect of wire diameter on the current density for 99.5% reduction in area is shown in Fig. 13 for drawn wires and Fig. 14 for etched wires. The large increases in current density which occur with decreasing wire diameter show clearly that the critical current does not scale as the wire area for Nb_3Zr in this field range. A similar increase in properties with decreasing diameter was found for wires cold worked 99.85% and for a higher oxygen content alloy.

In order to show the effects more closely, the critical-current densities are plotted vs the wire diameter for a constant field strength of 25 kilogauss in Fig. 15. The data show that critical-current densities for etched wires are inversely proportional to the wire diameters. These results are independent of the starting gauge for etching. For wires cold drawn 99.5% to various gauges, 5 to 16 mils, these properties rise on a similar, but slightly higher, curve. Below 5 mils, the properties of the cold-drawn wires continued to rise but less rapidly than etched wires. The curve was extended to 28 mils by including some data from an experiment where the cold working was not held constant. The relatively small decreases in current density with increased cold working (Fig. 12), however, do not interfere appreciably with the major effect of diameter.

Part of the superconducting current is assumed to flow on the surface of the wire, either in the normal penetration depth or in a group of filaments which are more densely packed near the surface. The rest of the current is assumed to flow in filaments evenly distributed in the

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Fig. 13. Effects of Wire Diameter with Constant Amount of Gold Reduction.

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Fig. 14. The Effect of the Critical-Current Density of Variation of Wire Diameter Through Etching.

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Fig. 15. Critical-Current Density of Nb₃Zr at 25 Kilogauss vs Wire Diameter.

bulk of the wire. Then for wire diameters, large compared with the depth of the surface currents, the current density can be expressed as

$$\frac{j - j_b}{j_s - j_b} = \frac{4\Delta}{d} \quad d \gg \Delta, \quad (1)$$

where Δ is the thickness of the surface layer and the current densities, j_s and j_b , of the surface and the bulk are functions of the external field. The current density should be a linear function of the reciprocal of the diameter. As the wire diameter approaches twice the thickness of the surface layer, the current densities become parabolic in $1/d$ and

$$\left. \begin{aligned} \frac{j - j_b}{j_s - j_b} &= \frac{4\Delta}{d} \left(1 - \frac{\Delta}{d}\right) \\ \frac{\partial j}{\partial \frac{1}{d}} &= 4\Delta \left(1 - \frac{2\Delta}{d}\right) (j_s - j_b) \end{aligned} \right\} \quad d > 2\Delta \quad (2)$$

$$\left. \begin{aligned} j &= j_s \\ \frac{\partial j}{\partial \frac{1}{d}} &= 0 \end{aligned} \right\} \quad d \leq 2\Delta \quad (3)$$

As shown in Fig. 16 for the drawn wires and Fig. 17 for the etched wires, the experimental data obey this relation fairly well - the current density being linearly proportional to $\frac{1}{d}$ at large diameters and becoming parabolic as $\frac{1}{d}$ increases.

The proportionality of the current to diameter can be explained in other ways. Shoenberg has suggested that filament densities could vary, as $\frac{1}{r}$ for example. Also, an arrangement of currents in thin concentric shells would scale with diameter. Surface currents are assumed because they are reasonable physically.

The experimental curves in Fig. 17 for etched wires when fitted to the Eqs. 2 and 3 show the following approximate values:

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Fig. 16. Critical-Current Density of Cold Drawn Wires vs Reciprocal Wire Diameter.

Fig. 17. Critical-Current Density of Etched Wires vs Reciprocal Wire Diameter.

External Field (kilogauss)	j_s (10^5 amp/cm 2)	j_b (10^5 amp/cm 2)	Δ (10^{-4} cm)
0	18	0	11
2	14	0.7	10
4	10	0.4	10
10	7	0.3	6
15	7	0.2	5
20	7	0.1	4
25	4	0.1	6

As shown in the tabulation, the major part of the current is carried in a layer at the surface of the wire with a thickness at least an order of magnitude greater than the usual penetration depth. The reason for this behavior in hard superconductors is not presently understood but it is assumed that the lower symmetry at the surface, or free-energy conditions arising from the interaction between currents, or bulk superconducting regions may restrict the continuous filaments to the surface of the wire. The limiting current densities to be obtained for very small wires (approximately 0.3 mil) and for alloys with this particular level of oxygen and carbon are then the values of j_s in the tabulation.

The cold-drawn and ground wires have the same properties as the etched wires for large diameters as shown in Fig. 16 where the dashed line represents the characteristics of the etched wires from Fig. 17. At the smaller diameters, however, the current densities of the drawn wire fall below those of the etched wire. This may be understood in a simple way if one assumes that fundamental size effect is that observed in the etched wires. The smaller critical-current densities of the cold-drawn or ground wires at the smallest diameters are then due to a damage effect arising from excessive amounts of cold work at the surface. This is not unreasonable as the reduction in area in each drawing pass increased as the final wire diameter decreased, and the surface cold working of grinding operations is well known. If this is

the case and means can be found to fabricate wires without these damaged surfaces, the higher critical-current density observed in small etched wires may be achieved by wire drawing.

An alternate interpretation of the higher critical-current densities of etched wire is that the etched wires were contaminated with hydrogen and a surface layer of better superconducting properties was formed. The cold-drawn wires rise in critical-current density because of a high property surface layer resulting from the wire-drawing process. This interpretation is unlikely, however, because one would expect decreases in critical currents upon removal of the outer layer. As shown in Fig. 16, grinding away the outer surface gave nearly the same results as wire drawing. Similarly, etching increased rather than decreased the critical-current densities. In the $\frac{1}{d}$ range 25 to 50, this occurred at nearly the same rate as in wire drawing. The changes in critical-current density with etching were independent of the etching reagent and of the time of etching in contrast to what would be expected if the wire were being contaminated during etching. As shown in Fig. 17, no significant differences were observed with changes in starting gauge. The difference between etched, cold-drawn, and ground wire, therefore, is believed to be due to cold-working surface damage in the latter wires.

Recently, Hauser and Buehler¹⁷ have developed a theory of hard superconductors with the dislocation as the basic element in the filamentary structure. The condition that the dislocation filament must form a continuous network throughout the length of superconductor reduces their number to values smaller than normal dislocation densities. The filaments are considered independently with sharply peaked distributions of current, radii, and critical fields. Hauser and Buehler's fundamental equations for such filaments are as follows:

$$I = 5r(H_{cf} - H_a) \quad (4)$$

$$j = \rho I, \quad (5)$$

¹⁷J. J. Hauser and E. Buehler, Phys. Rev. 125, 142 (1962).

where I is current; r is the radius; H_{cf} is the critical field of the filaments; ρ is the number of filaments per square centimeter; and j is the critical-current density.

The above theory will be applied to the present data without assuming, as Hauser and Buehler did, that distributions of filaments are homogeneously distributed throughout the volumes or that a distribution of critical fields occurs because of the angle between the filament and the applied field. The latter does not seem reasonable for $l \gg d$ since a continuous filament is bound to be normal to the transverse applied field at one place and this is assumed to be the critical region where the current field and the external field are parallel and add as magnitudes.

Substitution of Hauser and Buehler's Eqs. 4 and 5 into the previous Eq. 2 for a superconductor with an outer surface layer of improved properties gives the critical-current density as follows:

$$j = [\rho_b + (\rho_s - \rho_b) \frac{4\Delta}{d} (1 - \frac{\Delta}{d})] [5r(H_{cf} - H_a)] \quad d > 2\Delta, \quad (6)$$

where ρ_s and ρ_b are the dislocation filament densities of the surface layer and of the core of the wire. The current density according to this equation would be linear in H_a if ρ_s and ρ_b were independent of H_a . This would, of course, be incorrect as the j vs H_a curves are not linear but have a flat region at intermediate-current densities.

Hauser and Buehler, however, explain the plateau region, where j is nearly constant with H_a , by a decreasing density of filaments as H_a decreases. The decreasing density of filaments will be attributed in the present case to increasing current interactions between filaments.

Using the values given previously for Δ , j_s , and j_b and assuming $H_{cf} = 71,000$ gauss, $r = 10^{-7}$ cm, and equal values of I in the core and the surface filaments, the filament densities ρ_s were obtained from Eqs. 4 and 5 for the data of Fig. 17.

H_a (Kilogauss)	I (amp/filament)	ρ_s (10^7 dislocations/cm ²)	Average Spacing (A/filament)
0	0.036	5.1	1800
2	0.035	4.0	2600
4	0.033	2.9	3400
10	0.031	2.4	7300
15	0.028	2.4	9200
20	0.026	2.5	9900
25	0.023	1.9	9200

The filament densities are sufficiently small so that surface layers of the type proposed are reasonable physically. The last column shows the spacing between filaments in A units for the hypothetical situation that the filaments are in a monolayer and are parallel to the axis of the wire. The low-filament densities are characteristic of the Hauser and Buehler model - through the large currents per filament required to satisfy the conditions of their Eq. 4.

At low external fields, the rapid rise in ρ_s and also in j_s is believed to be due to the occurrence of bulk superconducting regions in the wire, either due to screening currents of the type discussed by Bean¹⁸ or due to those volumes of an inhomogeneous bulk superconductor which seem to permit much higher critical fields than the ideal bulk critical field. The screening model due to Bean does not, however, provide a simple explanation of the present size effects since this model would predict increasing values of Δ with increasing field while the opposite change in Δ was observed.

Hauser and Buehler show that at still lower fields the ideal bulk superconducting behavior will be assumed. This is so only if the following order is found in this inequality

$$H_{cb} - 2H_a > 2\rho_s \Delta \pi r (H_{cf} - H_a) \quad (7)$$

¹⁸C. P. Bean, Phys. Rev. Letters 8, 250 (1962).

The expression is for the present case of filaments in surface layer of depth, Δ . The other order of the inequality will lead to stabilization of filaments.¹⁹ Substituting the values, $H_{cb} = 2500$ gauss, $\rho_s = 4 \times 10^7$ dislocations/cm², $\Delta = 10^{-3}$ cm, $r = 10^{-7}$ cm, and $H_{cf} = 71,000$ gauss, the above expression shows that ideal superconductor behavior would be assumed at $H_a < 360$ gauss.

In Fig. 17, a dashed line has been drawn on the zero field curve according to the current formula for an ideal bulk superconductor

$$j\left(\frac{\pi d^2}{4}\right) = i = 5H_{cb}\left(\frac{d}{2}\right) \quad (8)$$

The value of H_{cb} for Nb₃Zr obtained in this way is 2230 gauss which is in reasonable agreement with the value of 2500 gauss reported by Hulm.²⁰

In conclusion, the size effects have indicated that very small wires, particularly those prepared with an etched surface, may have considerably increased critical-current densities. By carefully combining the small-wire diameters with controlled additions of interstitial elements and by precipitation heat treatments in such materials followed by smaller amounts of cold reduction, future Nb₃Zr wire superconductors with increased critical-current densities should soon be realized. From the fundamental standpoint, a study of size effects at higher fields than 25 kilogauss would be of interest to further show the nature of the superconducting current flow in niobium-zirconium wires. The Hauser and Buehler dislocation model accounts for the zero-field ideal superconducting behavior in Nb₃Zr and leads to reasonable filament densities in the surface layer. It does not, however, account for the existence of the surface currents or for the nature of the j vs

¹⁹The importance of the second inequality was pointed out by Jan Korringa. For the case where the filaments are uniformly distributed and with no external field, the inequality depends upon filament density, ρ , and wire diameter, d . $H_{cb} = \frac{1}{2}\rho\pi drH_{cf} + \delta$. If $\delta < 0$, filaments persist after the bulk quenches. Hauser and Buehler did not recognize the importance of the second inequality in their paper.

²⁰J. K. Hulm, M. J. Fraser, H. Riemersma, A. J. Venturino, and R. A. Wien, Proceedings of the International Conference on High Magnetic Fields, Cambridge, 1961 (Massachusetts Institute of Technology press and John Wiley and Sons, Inc., New York, 1962), pp 332-40.

H_a curve between zero field and the plateau region. The possibility of ideal bulk behavior to fields beyond 25,000 gauss exists and would account for the size effects with only the larger penetration depth, Δ , to be explained. This may be simply a matter of surface roughness. Future experiments to establish the fraction of superconducting volume of Nb_3Zr cold-worked wires are needed.

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