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# STUDIES ON FILAMENTARY $Nb_3Sn$ WIRES FABRICATED BY THE INFILTRATION METHOD

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# STUDIES ON FILAMENTARY $Nb_3Sn$ WIRES FABRICATED BY THE INFILTRATION METHOD*

K. Hemachalam and M. R. Pickus**

## ABSTRACT

Superconducting wires containing a network of $Nb_3Sn$ filaments are produced by powder metallurgy techniques. The fabrication involves achieving a controlled porosity in compacts of sintered niobium followed by tin infiltration and mechanical reduction. The $Nb_3Sn$ filaments, typically 1-5 µm in size, are formed by a short heat treatment. The effects of heat treatment on critical current and transition temperature are presented for reaction temperatures in the range of 700-1200°C and for lengths of time varying from 1 min to several hours. The dependence of $J_c$ on filament size is studied. The conductor evaluation includes measurements of $T_c$, of $J_c$ up to 170 kG, and mechanical bend tests. Efforts are made to explain the results, wherever possible, by means of microstructural observations such as the $Nb_3Sn$ grain size and the microvoids formed as a result of diffusion treatment. In view of the high values of $J_c$ obtained--$1.1\times10^5$ A/cm$^2$ at 100 kG and $7.5\times10^4$ A/cm$^2$ at 150 kG (computed on the basis of the $Nb_3Sn$-Nb core)--these filamentary wires appear to have a potential especially for applications in high field superconducting magnets.

## INTRODUCTION

Stability requirements and the inherent brittleness of A-15 superconducting materials have led to the development of special methods for fabricating these compounds into useable conductors. While several methods are still in developmental stages, the "bronze technique" has proven to be commercially attractive. However, the latter technique involves a repetitive bundling procedure followed by a long heat treatment in order to achieve a desired filament size. In addition, multifilamentary wires produced by this method appear to have a critical current density that falls off rapidly[1-3] at fields higher than 100 kG. This feature limits the full utilization of the high-field potential of A-15 compounds. With the idea of surmounting these shortcomings, powder metallurgy (P/M) techniques were employed to produce superconducting wires characterized by an array of $Nb_3Sn$ filaments in a ductile niobium matrix.[4,5] The objective of the present investigation was to determine the influence of different metallurgical variables on the superconducting properties in order to optimize the processing parameters.

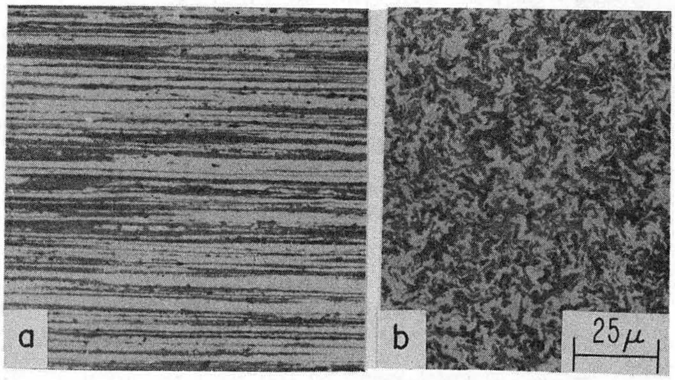


Fig. 1. (a) Longitudinal, and (b) cross sectional micrographs of reacted wire with 0.3 mm dia core.

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## PROCESSING OF WIRES

Niobium powder, 99.9% pure, and of particle size ranging from 37 to 44 µm, was isostatically compacted at 173-207 N/mm$^2$ (25-30 ksi) into self-supporting rods. These rods, 4 mm in diameter, were then sintered at 2250-2300°C for 10-15 min in a vacuum of $\sim6\times10^{-5}$ mm Hg. The porous sintered rods were cooled and infiltrated with tin by immersing them for 30 sec. in a tin bath maintained at 700°C. The infiltrated rods were ensheathed in a monel or copper tube with an intermediate cladding of annealed tantalum which served as a diffusion barrier. Mechanical reduction of these assemblies to wire by form rolling followed by wire drawing, resulted in the formation of tin filaments. The merits of different metal forming processes have been discussed elsewhere.[5] The superconducting filaments of $Nb_3Sn$ were formed by a diffusion heat treatment of wire specimens in an argon atmosphere. The diffusion temperature ranged from 700° to 1200°C while the duration varied from 1 min to several hours. Typical morphology of the $Nb_3Sn$ filaments in the reacted wires is illustrated in Figs. 1(a) and 1(b).

## SUPERCONDUCTING PROPERTIES

### Transition Temperature:

The superconducting transition temperature $T_c$ was inductively measured within an accuracy of 0.1°K. The critical temperature is taken as the temperature corresponding to the midpoint of the inductance change in the course of the transition. The $T_c$ of tantalum-clad wires is shown in Fig. 2 as a function of $Nb_3Sn$ formation temperature. The width of the transition, $\Delta T$, indicated by vertical bars, was defined as the temperature difference between 10% and 100% of the total

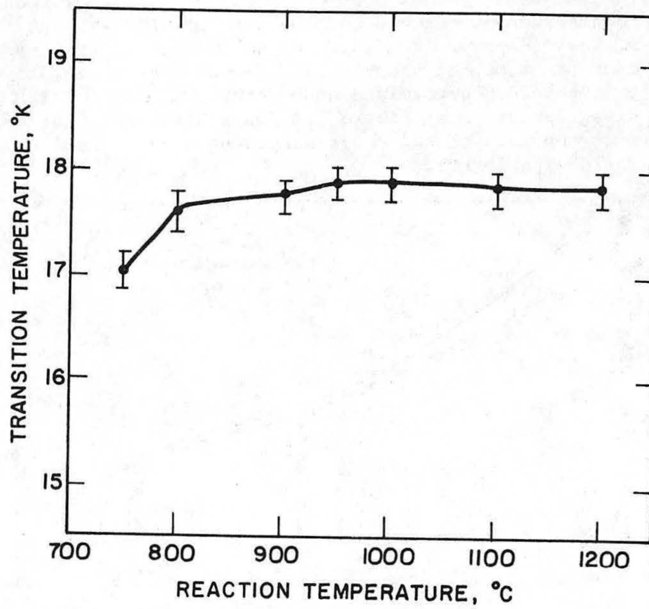


Fig. 2. Variation of transition temperature with the reaction temperature.

inductance signal. The 10% limit was chosen arbitrarily because the signal at the beginning of the transition changed gradually from superconducting to normal state.

In the temperature range 900-1200°C, the wires were heat treated for only 2 minutes. Three specimens treated for 1 hr at 750°, 800° and 950°C, respectively, had the same values of $T_c$ and $\Delta T$ as those heat treated for 2 min at the same temperatures. However, the longer reaction at 750° and 800°C resulted in an inductance signal greater than that corresponding to the 2 min durations. This is to be expected in view of the sluggish formation on $Nb_3Sn$ and the fast growth of other intermetallic compounds at these low temperatures. The absence of any noticeable change in the signal for specimens heat treated at 950°C for 2 min and 1 hr respectively, suggests that the formation of $Nb_3Sn$ had been completed in only 2 min.

In spite of the short heat treatment, the $T_c$ values plotted in Fig. 2 are in general agreement with those reported in the literature. The $T_c$ of the wires reacted above 900°C is 17.9±0.1°K, and it is not affected by reaction temperatures up to 1200°C. The observed decrease in the $T_c$ of specimens reacted below 900°C may be explained by the reduced atomic mobility necessary to achieve the crystallographic order[6,7] required for high $T_c$ in A-15 compounds.

Current Density

The influence of various metallurgical treatments on the critical current density of the P/M processed wires has been studied. The variation of critical current with magnetic field was obtained using a four point testing method in both pulsed fields (with a rise time of 8 milliseconds) and steady fields. As a result of uncertainties in estimating the volume fraction of the $Nb_3Sn$ phase, the current densities reported here were computed on the basis of the entire cross section of the infiltrated core (i.e., $Nb + Nb_3Sn$). Pulsed field values corresponding to the resistive transition for a given sample current were used for determining the critical current vs. magnetic field characteristics. In the case of tests performed under steady fields, the current densities were determined at a resistivity of $10^{-12}$ Ω-cm. Typical results, plotted in Fig. 3, show good agreement between the two sets of data at high fields. However, at fields below 50 kG, the critical currents measured under pulsed fields are low relative to the values determined under steady fields. This disagreement is attributed to Joule heating at the current contacts of the short sample used in the pulsed field experiments.

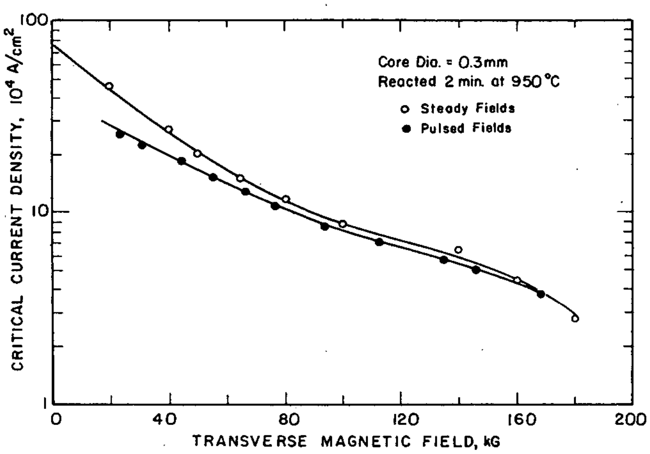


Fig. 3. Critical current density of the core as a function of magnetic field under pulsed and steady field conditions.

Effect of Heat Treatment: Wires clad with both tantalum and monel and having a core diameter of 0.3 mm were heat treated at temperatures in the range 700-1200°C. Figure 4 shows the field dependence of the current density of the core for 4 specimens reacted at 800°C for 2, 8, 30 and 120 min respectively. A substantial improvement in the critical currents with the increasing reaction time is apparent. These results are in general agreement with metallographic observations which show, for increasing reaction times, a progressive growth of the $Nb_3Sn$ layer. The specimen heat treated for 2 hrs at 800°C indicated a complete reaction of the tin. For these wires, the current density is surprisingly high in view of the reported fact that below 845±7°C, the peritectic temperature of $NbSn_2$, the diffusion reaction yields mainly $NbSn_2$ and traces of $Nb_6Sn_5$. The niobium-tin phase diagram[8] shows that none of the tin-rich intermetallics is stable above 930±8°C.

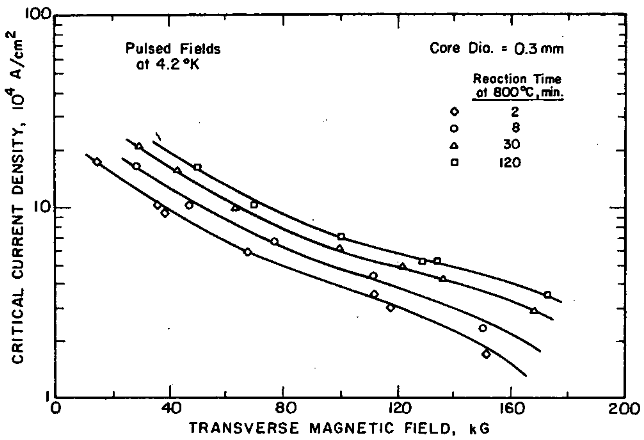


Fig. 4. Variation of current density with field for 0.3 mm-dia core wire reacted for different times at 800°C.

Since the rate of growth of $Nb_3Sn$ is also high above 930±8°C,[8] the formation of $Nb_3Sn$ is virtually completed in as short a time as 2 minutes. This can be seen from Fig. 5 in which the critical current densities are plotted for 7 specimens heat treated for times ranging from 1 to 60 min at 950°C. The 1-min heat treatment resulted in relatively lower current densities at all fields indicating an incomplete reaction. However, the other specimens with heat treatments of 2 min or longer have a similar current-carrying behavior. The slight scatter in the data points is within the experimental error limits of the tests under pulsed fields.

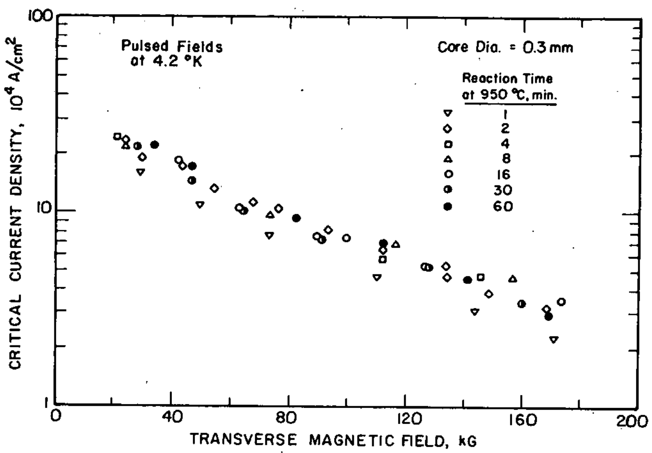


Fig. 5. Variation of current density with field for 0.3 mm-dia core wire reacted for different times at 950°C.

It is interesting to note that for specimens reacted at 950°C, the current density was not affected by prolonged heat treatments. Reaction periods up to 30 times the minimum required for a complete reaction have apparently had no detrimental effect on the microstructure of the $Nb_3Sn$ phase. This is consistent with a transmission electron microscope investigation (Fig. 6(a) and 6(b)) that reveals no noticeable grain growth when the reaction time is increased from 2 min to 30 minutes. The grains are nearly equiaxed with an average size of ~ 0.5 μm. In the General Electric tape which is formed by a similar diffusion reaction between liquid tin and niobium, a grain size of that order was achieved only by doping the niobium with zirconium.[9] In the P/M approach, the sintered niobium is severely cold worked prior to the final heat treatment. The dense dislocation network thus introduced in the niobium, (Fig. 6(b)), is believed to provide the nucleation sites for the formation of fine-grained $Nb_3Sn$.

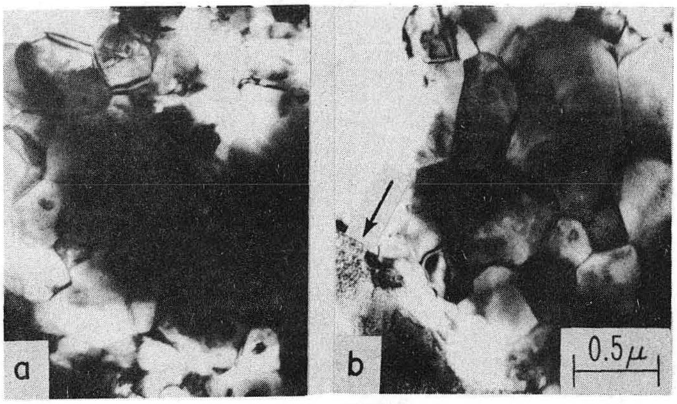


Fig. 6. Transmission electron micrographs showing $Nb_3Sn$ grains of specimens reacted at 950°C for (a) 2 min and (b) 30 minutes. The arrow indicates the region of dislocation in the niobium.

The variation of current density with reaction temperature is shown in Fig. 7 for three values of the magnetic field. The reaction times at 700°C, 800°C, and 900°C were respectively 50 hr, 2 hr, and 30 minutes. For temperatures of 950° and higher, the length of the heat treatment was 2 minutes. The metallographic study confirmed that the formation of $Nb_3Sn$ was practically complete in all the specimens. The $Nb_3Sn$ grains resulting from the reactions at 700°C, 800°C and 900°C were finer than those formed above 950°C. This grain refinement may be expected to enhance the critical current density. Instead, the current density is somewhat reduced (Fig. 7) in specimens heat treated at the lower temperatures. This behavior is believed to be associated with the lower $T_c$ values of these specimens. One can infer from the three curves in Fig. 7, that a heat treatment in the range 950-1000°C is optimal with respect to the critical current behavior of the present undoped wires.

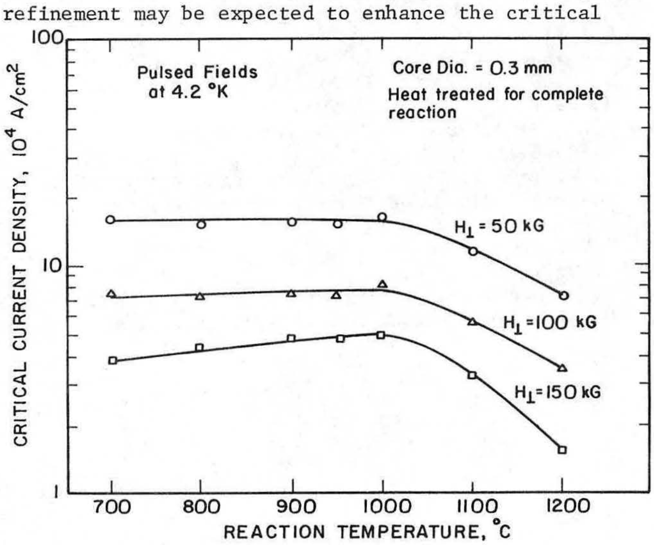


Fig. 7. Current density of 0.3 mm-dia core wire at 50, 100 and 150 kG as a function of reaction temperature.

Effect of Filament Size: Infiltrated rods, identical to those employed in the study of the diffusion heat treatment, were used to investigate the critical current dependence on the size of the $Nb_3Sn$ filaments. Filaments of different thicknesses were achieved by varying the amount of mechanical reduction in each wire. To ensure complete reaction, the wires were heat treated at 950°C for various times depending on the size of the central core. The strong dependence of the critical current on the amount of reduction is illustrated in Fig. 8. Here, the current densities at 50, 100 and 150 kG are plotted as a function of the square root of the reduction ratio R (R = cross sectional area of infiltrated rod ÷ cross sectional area of core in the final wire). Since the filament size is proportional to the core diameter (and, therefore, inversely proportional to $\sqrt{R}$), values of filament thickness determined from micrographs are also shown on the top scale of Fig. 8. The current density increases less than linearly with the inverse of filament thickness. For the best $J_c$ vs. H characteristics, the filament thickness in the present case should be less than ~ 1 μm.

The reaction treatment resulted in submicron pores dispersed in the superconducting phase. This porosity was a result of the molar volume difference between the $Nb_3Sn$ compound and the reacting components. The pores, 0.2-0.5 μm in size, were dispersed randomly in the thinner wires, while they appeared to cluster in the thicker ones. Reaction times, exceeding that necessary to convert all the tin into $Nb_3Sn$, did not result in any change in the porosity. It is believed that these microvoids along with the grain boundaries effectively pin the flux lines, thus improving the $J_c$ vs. H characteristics.

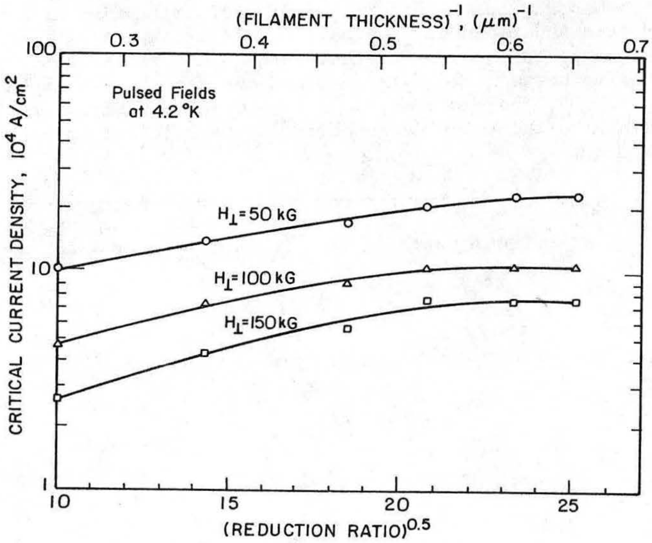


Fig. 8. Current density as a function of reduction ratio (and $Nb_3Sn$ filament size).

High Field Behavior: A noteworthy difference in the behavior of the P/M processed wires relative to those fabricated by other techniques is the reduced slope of the $J_c$ vs. H curves. This is illustrated in Table I in which the parameters, $J_c$(50 kG)/$J_c$(100 kG) and $J_c$(100 kG)/$J_c$(150 kG) for several $Nb_3Sn$ conductors, are listed.

Table I.

| Description | $J_c$(50 kG) / $J_c$(100 kG) | $J_c$(100 kG) / $J_c$(150 kG) | Reference |
|---|---|---|---|
| Internal bronze | 2.7 - 5.6 | † | 10 |
| External bronze | 3.3 | 4.2 | 1 |
| | 2.7 | 4.1†† | 2 |
| | 3.2 | 3.2 | 11 |
| GE diffusion processed tape | 2.6 | 6.7 | 12 |
| Filamentized tape | 2.4 | † | 13 |
| Infiltrated wire | 2.0 | 1.5 | Present work |

† Not available. †† Extrapolated.

The favorable values of the parameters, characteristic of the P/M processed wires, appear to be a result of the filamentary nature and the diffusion temperatures, higher than those employed in the bronze process. This feature is expected to make the present wires especially suitable for applications requiring fields in the neighborhood of 150 kG.

Mechanical Properties

The various operations such as cabling, braiding and coil winding, can easily degrade the current-carrying capacity of the filamentary wires. The decrease in critical current resulting from the bending of the wires was evaluated by wrapping 15 cm-long sections around a mandrel, straightening them and measuring the critical current. The same samples were bent around successively smaller mandrels. The tests were conducted at 4.2°K in a steady magnetic field of 50 kG perpendicular to the transport current. The critical current $I_c(D)$ for a bend-diameter D, normalized to the initial current prior to bending, $I_c(\infty)$, is shown in Fig. 9 for 2 specimens. As the wrapping diameter was successively reduced, the voltage drop in the wires at the instant of sudden transition to the normal state gradually increased. This was due to the occurrence of microcracks in the brittle superconducting phase. These cracks, acting as resistors in the supercurrent paths, lead to current sharing between the filaments and the matrix. As shown in Fig. 9, the minimum diameter to which the wires can be bent without any degradation in the critical currents is 2 cm.

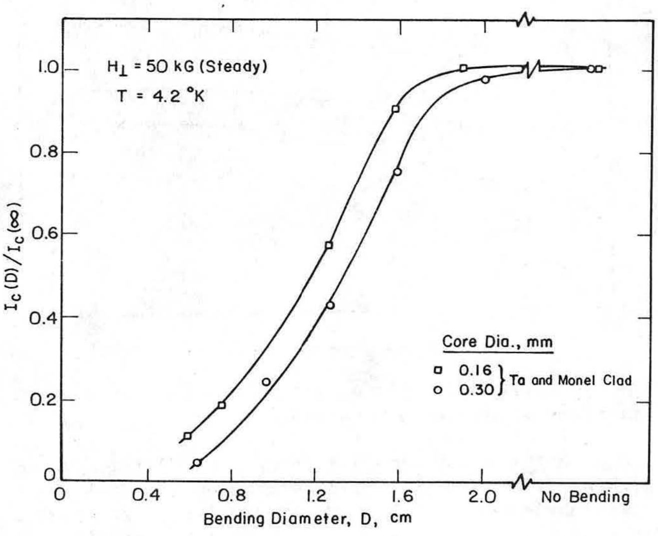


Fig. 9. Degradation of current-carrying capacity with bending diameter for two wires.

CONCLUSIONS

The potential of the P/M process lies in the possibility of adapting the techniques to other superconducting compounds, for example, $Nb_3Al$, $Nb_3Ga$, $V_3Ga$ and $Nb_3(AlGe)$.

In summary, the fabrication of flexible $Nb_3Sn$ filamentary wires with excellent current carrying capacity has been demonstrated. From the study of the microstructure and the superconducting properties, the following conclusions can be made: (a) The $T_c$ decreases with decreasing reaction temperature below 930°C. It is nearly constant at 17.9°K for reactions carried out between 930 and 1200°C. (b) The $J_c$ vs. H characteristics deteriorate rapidly when the heat treatment is performed at temperatures above 1000°C. (c) The times required for a complete reaction of the tin with the niobrium matrix at 700-800°C are of the order of hours while a 2 min treatment is sufficient at 950-1000°C. Once the formation of $Nb_3Sn$ is complete at a given temperature, the $J_c$ is fairly insensitive to further increases in the duration of the heat treatment. The latter conclusion is supported by studies of grain growth. (d) Reaction temperatures in the range 700-900°C (i.e., below the peritectic temperature of $Nb_6Sn_5$) result in current-carrying capacities comparable to those obtained above 930°C. (e) The $J_c$ increases with decreasing filament thickness down to about 1 μm below which there is a tendency toward leveling off. (f) The minimum diameter to which the wires can be bent without any degradation in the critical currents is 2 cm. (g) The $J_c$ of the present wires falls off more gradually above 100 kG than that of bronze processed multifilamentary wires.

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