Increased critical current density in Nb–Ti wires having Nb artificial pinning centers

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(Received 4 October 1996; accepted for publication 9 December 1996)

Artificial pinning center (APC) wires containing Nb 47 wt.% Ti with 24 vol.% of round Nb pins have produced very high critical current densities (J_c) which are attributed to a sharply defined, nanometer-scale Nb-pin array. By reducing both the number of warm extrusion steps from four to three and the temperature of the third extrusion from 650 °C to 250 °C, the degree of pin-matrix interdiffusion has been reduced and J_c values at all applied magnetic fields increased by 25–45% over those for a previous composite of almost identical design. The best wire achieved the very high J_c (5 T, 4.2 K) value of 4600 A/mm². These results underscore the importance of the thermomechanical treatment in determining the maximum flux pinning properties of APC Nb–Ti wires. © 1997 American Institute of Physics. [S0003-6951(97)02407-8]

The critical current density (J_c) of conventionally processed Nb 45–55 wt. % Ti wire is limited by the amount of normal conducting α -Ti precipitate that can be developed during thermomechanical treatment of the β -Nb–Ti alloy. Optimum flux pinning is achieved when the α -Ti precipitates are drawn to 1–2 nm in thickness.¹ J_c increases linearly with the volume fraction of α -Ti,² but there appears to be a kinetic and/or thermodynamic limit of ~ 25 vol. % of α -Ti in Nb 47 wt. % Ti. In order to overcome this apparent limit to the conventional process, artificial pinning center (APC) designs³ have been implemented which allow, in principle, for complete control over the pinning center composition, spatial arrangement, and volume fraction. Nb has been the most widely studied APC material, primarily because Nb is mechanically similar to Nb–Ti and because Nb-pin composites have produced the highest J_c values thus far. Most notably, an APC composite using a multilayer-sandwich design of Nb 50 wt. % Ti matrix and 28 vol. % of Nb pins⁴ achieved J_c (5 T, 4.2 K) of 4250 A/mm², distinctly higher than the maximum J_c (~ 3700 A/mm²) achieved conventionally.

While the thermomechanical processing steps^{5,6} and the resulting flux pinning nanostructures^{1,5} of high J_c conventional Nb–Ti wire are firmly established, the same is not true for APC wires. Consequently, it is not surprising that a significant range in J_c (H) is found for APC composites of nominally the same composition but manufactured via different processing routes. For instance, three groups have manufactured and characterized APC composites of Nb 47 wt. % Ti with 24–25 vol. % of nominally round^{7,8} or planar⁹ Nb pins. They produced maximum J_c (5 T) values of 2400, 3200, and 2800 A/mm², respectively. Although hard evidence is lacking, it seems likely that the range in J_c originates from differences in the flux pinning nanostructures. As recent work by Jablonski *et al.*^{10,11} has shown the detailed nanostructure of the pins exerts an important effect on the attainable J_c , independent of the vol. % of pin and its composition.

A very important difference between conventional and APC Nb–Ti lies in the evolution of the flux pinning nanostructures during processing. Conventionally processed Nb–Ti alloy becomes two phase late in its processing and only room-temperature wire drawing is necessary to reduce the two-phase microstructure down to optimum flux pinning thickness (1–2 nm). APC wires, on the other hand, are two phase throughout fabrication and some elevated temperature processing is generally unavoidable. So far, all practical APC composites require 1–4 warm extrusion steps, usually done at 550–650 °C. Interdiffusion associated with elevated temperature processing can mix the pin and matrix materials, weakening the sharpness of the designed two-phase nanostructure.

Studies by Kanithi *et al.*¹² and Heussner *et al.*^{8,13} have shown that the ultimate J_c (H) behavior of APC wires containing Nb 47 wt. % Ti with Nb pins was very sensitive to the number of warm (~ 600 °C) extrusions used in their fabrication. In our study,⁸ for the same nominal pin diameter, a wire which had received three 650 °C extrusions exhibited dramatically different $J_c(d_p, H)$ behavior compared to that for a wire which had received a fourth extrusion. Below 4 T the three-extrusion wire had higher critical current densities, while above 5 T the reverse was seen. As we could detect no difference in the average pin thickness or the pin thickness distribution at the optimum flux pinning size ($d_p = 40$ nm) for either composite, we attributed the different $J_c(d_p)$ behavior to pin/matrix interdiffusion caused by the fourth extrusion. Since interdiffusion should reduce the pin proximity length (ξ_N) by alloying the Nb, this should lead to the elementary pinning force (f_p) reaching its peak for thinner pins,¹⁴ thus raising the density of pins at maximum f_p , and enhancing the bulk pinning force (F_p) at higher fields where higher J_c is most desirable. However, such interdiffusion should also diminish the composition gradient at the pin/matrix interface, thereby decreasing the strength of f_p . Thus interdiffusion can have two opposing effects, making the quantitative impact on J_c unpredictable.

In order to directly address the influence of the sharpness of the pinning well on the strength of f_p , we decided to fabricate a new, nominally identical Nb 47 wt. % Ti/Nb APC composite but this time using lower temperature processing.

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We reduced the number of warm extrusions from four to three and the temperature of the last extrusion from 650 °C to 250 °C.

The composite was fabricated using the same rod-based APC method described earlier.⁸ Thirty-one 1-mm-diam. rods of Nb were arranged in a hexagonal array within 96 rods of Nb 47 wt. % Ti, such that the center-to-center pin spacing was $1.82d_p$ where d_p is the nominal pin diameter defined by:

$$d_p = d_w / \sqrt{N(1+R)}, \quad (1)$$

where d_w is the wire diameter, N is the number of stacked rods, and R is the copper to superconductor volume ratio. The hexagonal-shaped 127 rod stack was canned in Cu, evacuated, and hydrostatically warm extruded at 650 °C using a 15:1 area reduction ratio. The extruded wire was cut into 127 filaments, the Cu was etched off, and the hexagonal-shaped filaments were re-stacked, canned in Cu, and extruded under the same conditions. A third stack of 55 filaments was extruded at 250 °C using a 10:1 area reduction ratio. This final warm extrusion brought the nominal pin diameter down to 1.3 μm . The resulting wire was re-stacked with the Cu left on so as to produce a wire with seven superconducting filaments, each filament containing $31 \times 127 \times 55$ pinning centers. The wire was drawn to various sizes down to 0.08 mm diameter. Transport critical current (I_c) measurements were made at 4.2 K in liquid helium with the magnetic field applied perpendicular to the wire axis and a voltage tap spacing of 22 or 33 cm. I_c was defined using a 10^{-14} $\Omega\text{-m}$ resistivity criterion applied over the entire wire cross section. J_c was determined by dividing the I_c by the superconductor (Nb-Ti and Nb) cross-sectional area. The Cu-to-superconductor-area ratio was determined by weighing a length of wire, etching off the Cu, and re-weighing.

Figure 1(a) shows a transverse cross-section of the APC wire at $d_p = 400$ nm. Each of the seven superconducting filaments shown contains 216,535 Nb pinning centers, several of which are shown in the accompanying field-emission scanning electron micrograph (secondary electron image) of Fig. 1(b). The contrast between the Nb and Nb 47 wt. % Ti was obtained by lightly etching with a mixture of 25% HNO_3 , 25% HF , and 50% H_2O . At this size, the nominally round pins have begun to deform into ribbons but the designed hexagonal symmetry of the pinning center array is still evident. The transmission electron micrograph of Fig. 1(c) reveals that by $d_p = 25$ nm (slightly smaller than the optimum flux pinning size of $d_p = 39$ nm) the round pins have transformed into ribbons whose thickness ranges rather broadly from ~ 1 to 15 nm. This ribbon-shape range parallels that observed in our earlier composite.¹²

Figure 2 shows J_c as a function of the nominal pin diameter at applied magnetic fields of 2–7 T for the two prior composites having three and four extrusions, respectively, and for the new three-extrusion composite. The new composite achieves significantly larger values of J_c . Successive peaks in J_c vs d_p can be seen at 42, 35, 29, 25, and 20 nm for fields of 2, 3, 4, 5, and 6 T, respectively. Higher field peaks above 6 T were not observed because wires with $d_p < 19$ nm have not yet been fabricated. The data in Fig. 2 make it appear that some further high field increase is possible. The

FIG. 1. (a) Cross-sectional view of the Nb-pin APC wire at a nominal pin diameter of ~ 400 nm. Each of the seven filaments shown contains 216,535 pinning centers, several of which are shown in the field-emission scanning electron micrograph of (b). At this size, still a factor of ten larger than the optimum flux pinning size, the round pins are beginning to change shape. By optimum size ($d_p = 25$ nm), shown in the transmission electron micrograph of (c), the pins have transformed into ribbons with a broad thickness range of ~ 1 –15 nm.

FIG. 2. J_c vs d_p at applied fields from 2 to 7 T. The filled symbols connected by continuous lines represent the present composite for which the last extrusion temperature was reduced. The smaller symbols connected by dashed lines are $J_c(d_p)$ data at 3, 5 and 7 T taken from a previous composite which had the same composition of Nb 47 wt. % Ti with 24 vol. % Nb pins, but had received higher temperature processing. Two data sets are shown, that from $d_p = 105$ –40 nm (open symbols) corresponds to a third extrusion composite, while that from $d_p = 60$ –15 nm (crossed symbols) corresponds to a fourth extrusion composite.

J_c properties establish a new benchmark value of 4600 A/mm² at 5 T, 4.2 K for any round wire of Nb–Ti alloy.

Comparison of the properties of the new and the older composites makes it clear that relatively modest changes in the thermomechanical treatment can exert a large effect on the $J_c(d_p, H)$ behavior. The dashed lines show the $J_c(d_p)$ behavior at 3, 5, and 7 T for the earlier Nb 47 wt. % Ti/ 24 vol. % Nb pin composites.¹² The data from $d_p = 105\text{--}40$ nm are from the composite which received three 650 °C extrusions; they follow the data of the new composite well, J_c rising as the pin size decreases to 40 nm. The data sets from $d_p = 60\text{--}15$ nm show that the earlier four-extrusion composite actually outperforms the new three-extrusion composite at larger pin diameters. However, the new composite outperforms the older one at all fields at smaller pin sizes. This seems to indicate that any potential benefit to the elementary pinning force caused by interdiffusion decreasing the pin proximity length is outweighed by a decrease in the sharpness of the pinning wells. However, a recent experiment¹⁵ shows that the pin proximity length¹⁴ does influence the flux pinning behavior, though the full details of its influence are not yet clear.

In any case, the processing refinements embodied in this new composite have significantly contributed to producing a critical current density at 5 T of 4600 A/mm², a value some ~10% higher than the previous benchmark developed in a multilayer-sandwich Nb/Nb 50 wt. % Ti composite,⁴ despite the present composite containing ~15% less pinning center. The final shape and thickness distribution of the pins is likely to be very important in determining the flux pinning properties because of the influence that these parameters exert on the proximity coupling of the pins to the matrix. Round Nb pins change shape drastically in ways dictated by the deformation characteristics and the grain structures of the pin and matrix materials.¹² Even with the additional processing refinements of this letter, the pin thickness at optimum size varied from ~1 to 15 nm, a broader range than is observed in conventional Nb–Ti.¹ A broad pin thickness distribution is believed to be detrimental to J_c .^{10,11} Thus further significant increases in J_c should be possible from more uniform artificial pinning structures, as is suggested by recent multilayer studies by McCambridge *et al.*¹⁶ and Kadyrov *et al.*¹⁷

In conclusion, we have studied the critical current density of Nb 47 wt. % Ti wires with 24 vol. % of nominally round artificial Nb pinning centers as a function of pin diameter and magnetic field. Very high J_c values were obtained

when interdiffusion between pin and matrix was minimized by using lower temperature thermomechanical processing. A high J_c (5 T, 4.2 K) for round wires of 4600 A/mm² was achieved for a nominal pin diameter of 25 nm. Transmission electron microscopy showed that the real pin shape was ribbon-like with a thickness which varied from ~1 to 15 nm.

This work was supported by the U.S. Department of Energy, Division of High Energy Physics. The authors are grateful to C. Bormio Nunes, L. Cooley, A. Gurevich, E. Kadyrov, W. Starch, A. Squitieri, and M. Pelletier for valuable experimental assistance and helpful discussions and P. Jablonski and P. Morris of Teledyne Wah Chang for donating the Nb–Ti rod. The scanning electron microscopy was partially supported through the Integrated Microscopy Resource (Madison, WI) which is supported through a NIH Biomedical Research Technology Grant.

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