NON-UNIFORM DEFORMATION OF NIOBIUM DIFFUSION BARRIERS IN NIOBIUM-TITANIUM WIRE

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Abstract -- A major source of extrinsic limitation to the critical current density in Nb-46.5wt.%Ti superconductors has been sausaging initiated by the formation of hard intermetallics of Cu-Ti-Nb at the Cu-superconductor interface during precipitation heat treatment. The main defense against this is the use of a diffusion barrier (normally Nb foil) between the Cu and the Nb-Ti. However, Nb barriers are permeable to both Ti and Cu and protection provided by a given barrier thickness is limited by the tendency of the barrier to deform in a non-uniform manner even prior to heat treatment. We have examined the effect of varying the starting Nb-Ti grain size on the uniformity of barrier thickness reduction during wire drawing. For all the wires tested the non-uniformity of the barrier increased with drawing strain and with increasing initial Nb-Ti grain size. We have also compared the barrier of cold drawn monofilament to that of warm extruded filaments. The extruded filaments have a significantly more non-uniform barrier.

I. INTRODUCTION

It is well documented that the critical current density (J_c) of Nb-Ti superconductors is controlled both intrinsically by the Nb-Ti microstructure and extrinsically by an axially non-uniform deformation of the filaments incurred during the drawing process. The necessary first step in raising J_c is to produce at least 15 volume percent of α -Ti precipitates by multiple heat treatments^[1,2]. This permits an intrinsically strong flux pinning interaction. J_c is observed to increase linearly with increasing strain after the final heat treatment^[3]. The intrinsic J_c is raised during drawing because ~100-200nm diameter α -Ti precipitates produced at heat treatment size are reduced to ribbons ~1-2nm thick separated by ~5nm. Beyond a strain of 3-5, J_c begins to fall off. The principal cause of this fall is seldom intrinsic to the flux pinning but is more generally the effect of an extrinsic limit being placed on the critical current (I_c) of each filament, as the filaments begin to deform non-uniformly.

An adverse effect of α -Ti precipitation heat treatments has been the formation of hard, brittle intermetallics near the Cu-Nb-Ti interface due to Cu-Nb-Ti reactions^[4]. The consequence of intermetallic formation is filament sausaging. Studies by High et al.^[5] show that sausaging increases with

increasing strain and extrinsically limits the J_c . To help control intermetallic formation, a Nb diffusion barrier is added to the Nb-Ti ingot prior to processing in copper^[6]. Present barriers are generally 2-4% of the filament area, this value representing a compromise between the need to protect the filament from reaction^[7] and avoiding too much dilution of the effective filament cross-section by Nb. However, between the time when the barrier is applied (when the Nb-Ti ingot is ~150mm in diameter), the first heat treatment (when the individual filament is ~200 μ m dia. in the case of SSC conductors) and the final filament sizes (6 μ m for SSC conductors), very large drawing strains of order 13 and 20, respectively, occur. It is a remarkable fact that uniform deformation of each filament is possible; however, Faase et al.^[7] have shown that the Nb barrier deforms rather non-uniformly. This local thinning of the Nb barrier permits nucleation of Cu-Nb-Ti intermetallics under the barrier. These instigate non-uniform deformation of the filament and thus impose an extrinsic limit on J_c . Thus a critical step in optimizing such barrier-clad composites is understanding why barriers deform non-uniformly, even prior to any precipitation heat treatment that they receive.

To study the process of barrier deformation, the physical properties which govern the Cu/Nb/Nb-Ti mechanical coupling must be examined. Nb46.5wt.%Ti can be retained as a bcc solid solution, Nb is also bcc, and Cu is fcc. In order for a composite of these 3 metals to reduce uniformly, there must be an accommodation between the bcc Nb and Nb-Ti and fcc Cu^[8,9,10]. Upon drawing, bcc grains tend to deform such that a <110> direction is aligned with the drawing axis. Upon further drawing, the bcc crystals deform under plane strain conditions and the grains become ribbon-like, thinning in a <001> direction. In order to maintain continuity at the grain boundaries, the grains must change shape, inter-curling around one another^[8,9,10]. By contrast, Cu deforms in an axially symmetric fashion and, because it is softer, can accommodate the textured plane strain deformation of the Nb-Ti. It is the non-uniform deformation of textured Nb and Nb-Ti which sets up the conditions for local thinning of the barrier.

II. EXPERIMENTAL DESIGN

Initial examination of SSC R&D composites indicated that most of the non-uniform deformation of the barrier occurred at the interface between the Nb barrier and the Nb-Ti. We suspected that the roughness of the barrier was determined by the starting Nb-Ti grain size. Initial experiments have therefore concentrated on the relationship between initial Nb-Ti

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Fig. 1 Barrier deformation for the largest original Nb-Ti grain size (23 μm) at (a) $\epsilon = 0$ (fully annealed), (b) $\epsilon = 0.96$, (c) $\epsilon = 2.8$, and (d) $\epsilon = 4.7$ (final strain). Figures 1d & e compare the barriers at the final strain for the largest and smallest (7 μm) grain sizes, respectively.

grain size and non-uniform deformation of the barrier.

The material used for this experiment was an SSC Phase II R&D monofilament that had been extruded from 7.25" overall diameter and cold drawn to 0.37" in diameter. The four layer Nb wrap was 60-70 μm thick at 0.37" diameter (Fig. 1a). Six samples of monofilament were used for the experiment. Five were given heat treatments to vary the Nb-Ti grain size, while the sixth was not heat treated. The latter one served as a benchmark for normal monofilament processing. Parekh^[11] has shown that Nb46.5wt%Ti does not recrystallize at 750°C and that grain growth initiates rapidly in the range of 800 - 900°C. At these temperatures, Nb46.5wt%Ti is well within the single phase β region, so no α -Ti is formed^[12]. Using Parekh's experimental constants for grain growth in Nb46.5wt%Ti, it was determined that heat treatments at 850°C for times ranging from 10 to 240 minutes would provide a wide range of grain sizes.

We were initially concerned that Cu and Ti might diffuse through the barrier to form intermetallics at elevated temperatures and that this might initiate non-uniform deformation of the barrier. Studies by Faase^[7] et al. show that at 850°C, the fastest diffusion step is that of Ti through Nb. This is contrary to temperatures below 630°C, where Cu diffusion through Nb is fastest. Using experimentally determined reaction coefficients^[7], it was calculated that Ti diffusion would be less than 1 μm for a 240 minute heat treatment at 850°C. This is negligible for the 60-70 μm thick barrier.

The heat treatments were done with flowing argon, followed by a cold water quench to halt grain growth and prevent α -Ti precipitate formation. The wires were drawn down to

0.036" diameter according to the usual schedule of 20% area reduction per die with samples taken after every other reduction. This corresponds to a final true strain (ϵ) of 4.7, where $\epsilon = 2 \ln [D_0/D]$. D_0 and D correspond to the last recrystallization and to the final cross-sectional diameters of the wire.

The five recrystallized samples were etched using a solution of composition 50ml HNO_3 , 20ml H_2O and 30g ammonium bifluoride in order to expose grain boundaries. Mean lineal intercepts ($\bar{L}$) of the grains were measured from optical micrographs. The mean grain diameters ($\bar{d}$) were calculated using the formula $\bar{d} = 1.128\bar{L}$ ^[13].

The drawn wire samples were etched using a mixture of composition 25% HF, 25% HNO_3 , and 50% H_2O to expose the Nb barriers. To measure the variability of the barrier thickness, it was necessary to take photographs of each barrier using both light microscopy and Scanning Electron Microscopy-Backscatter Electron Imaging (SEM-BEI), depending on the wire diameter. The micrographs were converted into binary images using the IA system. An IA program was developed that placed a matrix of 400-500 closely spaced, parallel lines perpendicular to the binary image of the barrier^[6]. The intercepts of these lines with the barrier edges were computed and the average thickness ($\bar{t}$) and standard deviation of the thickness (σ_{n-1}) were recorded.

As a final experiment, barrier deformation of the cold drawn monofilament was compared to that of the same monofilament which had been stacked at ~0.1" diameter and warm extruded (575 - 625°C) by the manufacturer. The monofilament was drawn down until the monofilament diameter was similar to that of the extruded filaments. Barrier

Fig. 2 $\sigma_{n-1}/\bar{t}$ % vs. ϵ for varying initial Nb-Ti grain size. The zero of strain is taken to be the recrystallization size of 0.37" diameter. Also shown is the difference in $\sigma_{n-1}/\bar{t}$ between the cold worked and extruded filaments. These latter two measurements have an additional prior deformation strain of 5.5, which should be added to the values quoted.

thickness measurements were made as described above.

III. RESULTS

The mean grain diameters of the heat treated Nb-Ti ranged from 7 μ m to 23 μ m. Figures 1a-d shows the deformation of the barrier in the sample with the largest initial Nb-Ti grain size after incremental amounts of cold drawing. Along with the grain boundaries, swirl patterns which intersect grain boundaries were observed in the annealed Nb-Ti. These swirl patterns result from the chemical segregation induced by the large miscibility gap of Nb46.5wt%Ti. It is apparent that the barrier thickness variability increases with increasing strain. Figures 1d & e compare barriers at final strain ($\epsilon = 4.7$) for the smallest and largest initial Nb-Ti grain sizes. Clearly the larger initial Nb-Ti grain size has the greater degree of uneven barrier deformation.

A plot of the coefficient of barrier thickness variation ($\sigma_{n-1}/\bar{t}$) vs. true drawing strain is shown in Fig. 2. A linear regression line can be usefully fit to each data set. Recrystallization markedly increases the barrier irregularity in quite a

systematic fashion. It is clear that the both increasing strain and increasing starting grain size have a deleterious effect on barrier uniformity.

The coefficients of barrier thickness variation for the cold drawn monofilament and the extruded multifilament are compared in Fig. 2. The barrier is almost 5 times more non-uniform in the extruded material and the coefficient of variation reaches 60% before any precipitation heat treatment is applied to the material.

IV. DISCUSSION

Figures 1a-d clearly demonstrate that a drawing texture develops in bcc poly-crystals and that this texture produces a markedly non-uniform Nb barrier. As seen in Figure 1b, at $\epsilon = 0.96$, the grains are just beginning to change shape as the $\langle 110 \rangle$ texture develops. With further drawing the grains become more deformed and the barrier becomes more uneven. By $\epsilon = 4.7$ (Figure 1d) massive inter-curling is required to maintain continuity at the Nb-Ti grain boundaries. From the photographs it is also apparent that most of the uneven barrier deformation is on the Nb-Ti side, rather than on the softer Cu side.

Degradation of the barrier with increasing strain and grain size is quantified in Figure 2. Heat treatment of the Nb-Ti which grows the Nb-Ti grains is clearly very destructive to the barrier, the spread in $\sigma_{n-1}/\bar{t}$ reaching as high as 35% after a strain of only 4.7 for an initial grain size of 23 μ m. Neither this strain nor this grain size is exaggerated, since recrystallized grain sizes of 40 μ m in Nb46.5wt.%Ti are those normally specified and the total deformation strain required for barrier-clad Nb-Ti is of order 20. This point is reinforced by comparing the data for the cold drawn monofilament and extruded filaments in Figure 2 (note that the strain axis for these two data sets has a different zero, as explained by the caption.) Without any heat treatment $\sigma_{n-1}/\bar{t}$ would be predicted to be ~17% at the first heat treatment filament size of ~200 μ m (this corresponds to a total strain of ~13). However, the extruded sample had a dramatically greater barrier non-uniformity, $\sigma_{n-1}/\bar{t}$ being 50-60%. Such filaments are clearly in grave danger of having their barrier become non-protective for the reasons already discussed by Faase et al.^[7]

The results of this study clearly show that barrier breakdown occurs by non-uniform deformation, which itself is a consequence of the deformation texture of bcc metals. The important point is to maintain uniformity across the barrier. In the present case, the Nb barrier grain size was never larger than 5 μ m when examined in the recrystallized samples, always smaller than the Nb-Ti grain size (the Nb grain size did not appear to vary with heat treatment time). Thus it is the Nb-Ti non-uniform deformation which determines the non-uniformity of the barrier deformation. This point is reinforced by Fig. 3 where the strain-normalized barrier non-uniformity ($\sigma_{n-1}/\bar{t}$ %)/ ϵ is plotted against the ratio of the recrystallized Nb-Ti

Fig. 3 $\sigma_{n-1}/t \% / \epsilon$ vs. Nb-Ti grain size to Nb barrier thickness ratio showing that the strain rate of uneven barrier deformation increases linearly with an increasing $(\bar{d}/\bar{t})$ ratio.

grain diameter to Nb barrier thickness. An excellent linear relationship is obtained. It is clear that there is every incentive to reduce the grain size of Nb-Ti with respect to the Nb barrier thickness and to be cautious about recrystallization of the Nb-Ti prior to multi-filament extrusion.

V. CONCLUSIONS

Quantitative image analysis shows that the coefficient of variation of Nb barrier thickness ($\sigma_{n-1}/t \%$) increases with increasing drawing strain and increasing Nb-Ti grain size. An increasing Nb-Ti grain size exerts a particularly deleterious effect on barrier non-uniformity, making it inadvisable to recrystallize Nb-Ti monofilaments at an intermediate size prior to stacking them in the multifilament billet.

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