The Influence of Filament Size and Atmosphere on the Microstructure and J_c of Round Multifilament $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ Wires

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Abstract—Round multifilament $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ wires having 37 and 259 filaments fabricated by the oxide-powder-in-tube method were given a step solidification partial melt heat treatment in air and oxygen atmospheres. Significant improvement in the critical current density (J_c) and as high as $1.65 \times 10^5 \text{ A/cm}^2$ at 4.2K zero field was obtained for samples treated in pure oxygen versus air anneals. Moreover, as the filament size decreased the J_c increased. In this paper we will discuss the development of 2212 microstructure and its dependence on filament size and heat treatment atmosphere in round multifilament 2212 wires.

I. INTRODUCTION

Ag-sheathed $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223) and $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ (2212) conductors have been extensively studied as leading candidates for wire and tapes. These have the potential to be fabricated in long lengths from which solenoid-type superconducting magnets can be manufactured.⁽¹⁻⁴⁾ To date, most efforts have focused on flat tape conductor designs in order to obtain a strong c-axis texture.⁽⁵⁻⁸⁾ Practical levels of critical current density (J_c) have been achieved in high magnetic fields at 30K in 2223 tapes made using the oxide-powder-in-tube (OPIT) method,⁽⁹⁾ and in 2212 dip-coated tapes at 20K.⁽¹⁰⁾ High temperature superconducting magnets have been fabricated from these tape conductors by winding pancake coils that are stacked to form solenoids. Although high J_c has been obtained in the magnetic winding, the J_c characteristics of the conductors are highly anisotropic and coil performance is limited by that component of the magnetic field perpendicular to the flat surface of the tape. This limitation becomes more significant in larger or more complex solenoids and at the higher temperatures required for economy of refrigeration.

For practical applications, a multifilament wire that is twisted so the filaments are transposed is desirable for low loss operation and for magnet field uniformity free of large induced magnetic moments. It is straight forward to uniformly twist a round 2212 wire before it is heat treated.

In this paper we describe further the microstructure and J_c results on OPIT, Ag-sheathed, round, multifilament 2212 wire as a function of the heat treat atmosphere and filament size. The effect of the filament diameter was first reported by Motowidlo et al.^(11, 12) on multifilament wires and by Wesche et al.⁽¹³⁾ on mono core wires. The OPIT process is inherently well-suited to the manufacture of long lengths of cable, or as rectangular monolithic conductors. In contrast to 2223, 2212 is melt processed and does not require multiple rolling and sintering steps. Thus, 2212 conductors can be drawn, twisted, cabled or shaped, and wound before the wire is heat treated to make the conductor superconducting. Thus, 2212 is well-suited to use the process developed for fabricating Nb_3Sn . In addition, because the melt processing for 2212 is relatively short and the fabrication steps are straightforward, conductor made by this process is expected to be less expensive than conductor made using the more complicated 2223 process.

II. EXPERIMENTAL DETAILS

Fabrication of the multifilament 2212 conductors was performed using the well known OPIT process. The Ag tubes (99.9%, 13.2 mm O.D., 11.7 mm I.D.) were filled (30% dense) with stoichiometric 2:2:1:2 precursor powder (Seattle Specialty Ceramic) then sealed with a Ag plug that was swaged in place. These billets were drawn on conventional fabrication equipment at IGC Advanced Superconductors in a similar fashion as performed on low temperature superconductors. To make the 37 filament wire, monocoil wires were drawn, then 37 wires were stacked and drawn. The 259 filament wire was made by restacking and drawing seven 37 filament wires. The final OD of the wires ranged from 0.37 to 1.02 mm. For the 37 filament design, wires with 30 μm , 60 μm , and 100 μm filaments were heat treated. For the 259 filament design, wires with 11 μm and 16 μm filaments were heat treated. In addition, some samples with 259 filament design were given a twist pitch of 4 per inch before heat treatment. In all cases, 20 cm long samples were heat treated. Figure 1 shows an example of a transverse cross section of wire with 259 filaments at final size before heat treatment.

The heat treatment used for all the wires is shown schematically in Fig. 2. This process is called step-solidification melt processing.⁽¹⁴⁾ The maximum processing temperature was 885°C, followed by cooling at 10°C/hr to 870°C where the sample was held for 24 hr. The temperature steps were 5°C and the times were 24 hr., through 840°C, after which the power was turned off and the

— Manuscript received October 28, 1994.

This work was supported in part by the US Department of Energy (DOE) Small Business Innovation Research (SBIR) Office under Grant DE-FG02-92ER81461 (IGC)

samples were furnace cooled.

After the heat treatment, 4 cm lengths of wire were cut from the 20 cm samples and carefully mounted on a four probe jig to measure the dc J_c . The J_c was measured from 4.2 to 60K at OT and in fields of 0.5 to 12T at 4.2K using a $1\mu\text{V}/\text{cm}$ criterion. Magnetization measurements were performed using a Vibrating Sample Magnetometer (VSM). The volume fraction of 2212 within the total wire area (for J_c calculations) was measured on images of unreacted cross sections using image analysis at the University of Wisconsin and by weighing enlarged optical micrographs at IGC Advanced Superconductors. These values were in reasonable agreement. The superconducting fraction in the

wires with 37 filaments was 35-40% and 25-35% for the wires with 259 filaments.

III. RESULTS AND DISCUSSION

The original step-solidification process was done in air on tapes.⁽¹⁴⁾ It was designed to align the 2212 grains and reduce the size of the residual $(\text{Sr,Ca})\text{CuO}_2$ (1:1 AEC [alkaline earth cuprate]) in the fully processed tape.⁽¹⁴⁾ In the present study it was extended to round multifilament wires processed in air, 50% O_2 and 100% O_2 using the original heating schedule. The overall cross sections for the heat treated wires in air and 100% O_2 is shown in Figures 3a and b.

Figure 1. Cross section of a 0.518 mm diameter multifilament 2212 wire (259, $16\mu\text{m}$ filaments) before heat treatment.

Figure 2. Thermal cycle in step solidification melt process of BSCCO-2212 wires.

Figure 3a. Cross section of a 0.518 mm diameter wire after an air step solidification melt process.

Figure 3b. Cross section of a 0.518 mm diameter wire after 100% O_2 step solidification melt process.

Further enhanced SEM micrographs of the wires' microstructure is shown in Figure 4, 5 and 6. The dominant phases present in Fig. 4 after heat treatment in air included $(\text{Sr, Ca})\text{CuO}_2$ (1:1)AEC, Bi-2212, and $\text{Bi}(\text{Sr,Ca})_2\text{O}_x$ (Cu-Free). The critical current for this sample was 28 Amps at 4.2K, zero field. In the case of 50% O_2 atmosphere, Fig. 5, the microstructure is characterized by the phases which include $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_x$ (14:24)AEC, Bi-2212, and Bi $(\text{Sr,Cu})_2\text{O}_x$ (Cu-Free). The critical current in this case was

25.7 Amps. Except for the difference in the AEC phases the microstructure and I_c 's for air and 50% O_2 heat treat were fairly similar. However, upon increasing the oxygen to 100%, a microstructure characterized by significant melt texturing and cross-linking that resulted in a synapse-like structure is shown Fig. 6. The predominant phases obtained after the 100% O_2 heat treat was Bi-2212 and minor or small amounts of Bi-2201 and Sr-rich phases. The critical current in this sample was 88 Amps.

Figure 4. SEM micrographs at a) 200 x and b) 1,000 x for melt processed wire in air. The dominant phases are A (1:1 AEC), B (Bi-2212), C (Cu-Free).

Figure 5. SEM micrographs at a) 200 x and b) 1,000 x for melt processed wire in 50% O_2 . The dominant phases are A (14:24 AEC), B (Bi-2212), C (Cu-Free).

Figure 6. SEM micrographs at a) 200 x and b) 600 x for melt processed wire in 100% O_2 . The dominant phases are A (Bi-2212), B (Bi-2201), C (Sr-rich phases).

The critical current density for air and 100% O₂ is summarized in Fig. 7. In general we found significantly higher J_c for wire processed in O₂ regardless of filament size. These results are consistent with previously reported work on flat Ag-sheathed monocoil Bi-2212 tape.⁽¹⁵⁾ Here they found that in O₂ the residual phase was (Sr,Ca)₁₄Cu₂₄O_x (14:24 AEC) rather than 1:1 AEC, which was present when processing in air. The 14:24 AEC grains were much smaller than the 1:1 AEC grains, which correlated with the higher J_c in wire processed in O₂ than in air.⁽¹⁵⁾

Figure 7. J_c as a function of inverse filament diameter for wires heat treated in air and pure O₂. The samples processed in pure O₂ have the higher J_c .

The present results for round multifilament wires suggest that both the processing atmosphere and filament size are important parameters for controlling J_c . A plot of the J_c as a function of the inverse filament size for wires heat treated in 100% O₂ (Fig. 8) shows that the J_c increases with decreasing filament size. The highest J_c (165,000 A/cm² 4.2K, OT) was achieved in wires with the finest filaments (11 μm). The critical current (I_c) in this 0.368 mm OD wire was 45 A yielding an engineering critical current density of 42,308 A/cm². We also found that the spread in J_c increased with decreasing filament size. We believe this J_c variation may be due to mechanical damage the finer wires experienced during mechanical deformation. For instance, we observed that the smaller wire sizes "stretched" due to excessive tension applied to the wire during the drawing operation. The low yield strength, (about 31 MPa) of round, Ag-sheathed, multifilament 2212 composite wire increases the likelihood for stretching, which may break the filaments.

Figure 8. J_c as a function of inverse filament diameter for wires heat treated in pure O₂. The J_c increases with decreasing filament size.

In addition to the transport measurements, magnetization measurements were also performed on all wires with filament diameters (100 μm–11 μm) shown in Fig. 8. The M-H loop closure was used to determine the irreversibility field, H_r , as a function of temperature for all wires with J_c 's ranging from 12,000 A/cm² to 165,000 A/cm². The irreversibility fields $H_r(T)$ for various wires shown in Fig. 9 suggest that the increase in J_c (transport) with decreasing filament diameter is largely due to extrinsic factors and not due to mechanically induced flux pinning.

Figure 9. The irreversibility field, H_r , as a function of temperature for samples with transport J_c ranging from 12,000 to 165,000 A/cm².

Additionally, Fig. 10 compares the wire data displayed in this way with that of high quality single crystals of Bi-2212 prepared by float zone process. The data is intermediate between those of the single crystal Bi-2212 data for $H_{||}$ and $H_{\perp}$ orientations. This reinforces the conclusion that the flux pinning in those wires is similar to that of single crystals.

Figure 10. A comparison of H_c for 2212 wires and 2212 single crystals with $H_{\parallel}$ and $H_{\perp}$.

Previous experimental work suggested that the c-axis alignment of the 2212 is promoted by the Ag sheath.⁽⁵⁾ Other groups observed high c-axis alignment in 2212 thick films on MgO within 10 μm of the MgO interface, but poor alignment at air interface in 40 μm thick films.⁽¹⁶⁾ Ray⁽¹⁴⁾ and Hellstrom⁽⁸⁾ developed a model that describes the alignment mechanism for 2212 in two-dimensional tapes and is independent of the substrate material. Their model can be extended to one dimensional filaments where the c-axis in the 2212 grains is expected to be radially aligned around the filament axis, and smaller filaments are expected to have higher alignment than larger filaments. In the present work, neutron diffraction pole figures of wires with 60 μm filaments showed radial c-axis alignment in agreement with the predictions.

IV. CONCLUSION

We have fabricated Ag-sheathed, round multifilament 2212 wire with 37 and 259 filaments. The J_c was highest for wires heat treated using step-solidification melt processing in pure O_2 atmosphere. J_c also increased with decreasing filament size. The combination of step-solidification melt processing in O_2 , and small filament size yielded the highest J_c of 165,000 A/cm^2 (4.2K, OT). Measurements of J_c on these round wires as a function of temperature and magnetic field suggest that 2212 can be used in device applications at temperatures up to 20K.⁽¹²⁾

Due to the large number of parameters involved, completely optimized conditions for processing Ag-2212 wires have not been realized. However, further improvements in the superconducting properties of the wires and their reproducibility is expected with optimization in conductor design as well as drawing and heat treatment schedules. These could then lead to uniform properties in long length, multifilament wires.

This work was supported by the Department of Energy

through the SBIR program under grant number DE-FG02-92ER81461, the Electric Power Research Institute contract number RP8009-05, and the Advanced Research Project Agency contract number N00014-90-J-4115.

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