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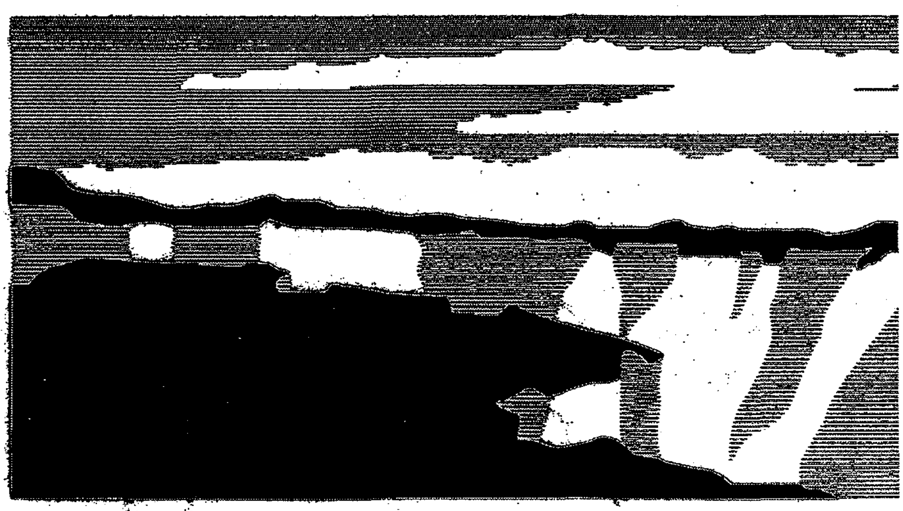

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Bi-2212 AND Bi-2223 WIRE DEVELOPMENT

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ABSTRACT

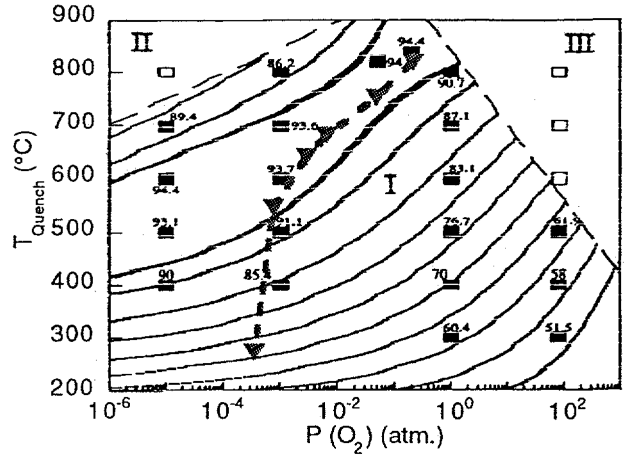
The results of innovative processing of Bi-2212 by isothermal melt processing and by controlled oxygen pressure cooling yield improved properties over the conventional routes. The addition of large grains of Ag has resulted in improved core/interface geometry and better performance in Bi-2212 and Bi-2223. A deformation processing study of Bi-2223 showed the effects of sheath material, relative core thickness, and reduction per pass on core/interface uniformity.

INTRODUCTION

Processing of high temperature superconductor (HTS) materials for power applications, such as motors, generators, magnets, and transmission lines, has focused primarily on the Bi-based superconductors $Bi_2Sr_2CaCu_2O_x$ (Bi-2212) and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ (Bi-2223) manufactured as a thick film coating on Ag or by the oxide powder in Ag tube (OPIT) process. These are the only HTS materials which can be processed into a long conductor with good intergranular current transfer. Some aspects of the thermomechanical processing of these materials which lead to improved critical current density performance are discussed below.

CONTROLLED pO_2 PROCESSING OF Bi-2212/Ag TAPE

If Bi-2212 tape is slow (furnace) cooled from its anneal temperature to room temperature, then the sample picks up excess oxygen which reduces T_c and promotes decomposition of Bi-2212 at the grain boundaries. These samples carry less current than samples quenched quickly from the anneal temperature. However, it is not possible to quickly cool large coils from the anneal temperature. If attempted, the process will likely yield non-uniform properties in the tape due to large temperature gradients within the furnace and coil. It is desirable to cool coils slowly to maintain uniform properties while avoiding T_c and J_c degradation. Triscone *et al.* reported that pO_2 and temperature could be varied together to maintain high a T_c.[1] This technique has been applied here to maintain optimum pO_2 conditions during cooling of Bi-2212 samples in a large 3-zone furnace to produce high performance, slowly cooled samples. The best results have been achieved with a heat treatment consisting of the following: 1. Ramp to a maximum temperature of 902°C in 83-100% O_2/Ar gas, cool at 240°C/h to the 853°C anneal temperature. 2. Switch to 21-23% O_2/Ar when the anneal temp is reached. 3. Anneal for an extended time of 80 to 100 h. 4. Conduct pO_2/Temp cooling as shown in Fig. 1. Figure 2 shows the best J_c obtained at 4 K of 214 kA/cm^2 and I_c of 93 A. An I_c of 10 A was obtained at 75 K, self-field. These results show that it is not necessary to cool to low temperatures very rapidly, which is difficult to accomplish in a large furnace, in order to avoid decomposition of the Bi-2212 phase material.



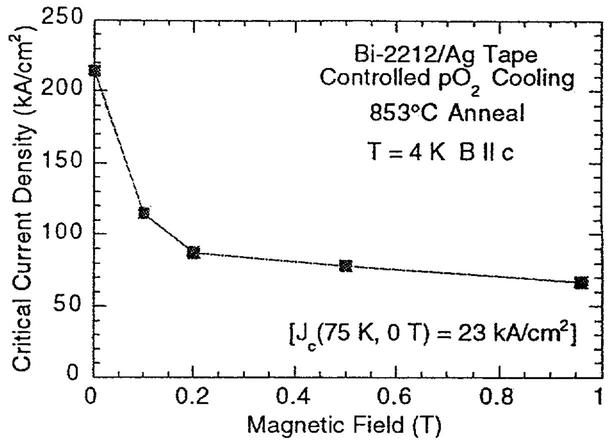
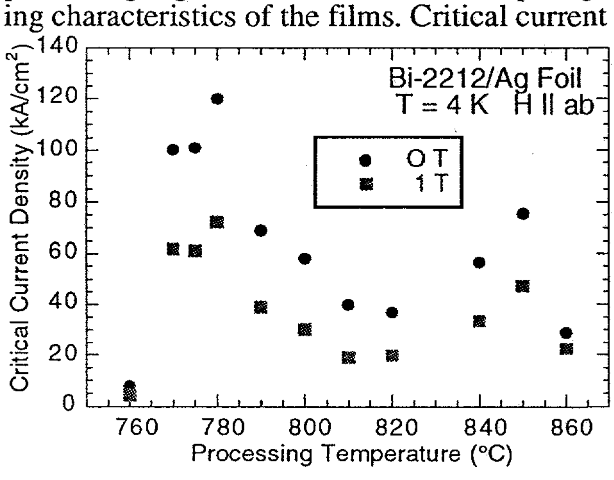


Fig. 1. Quench temperature *vs.* pO_2 for Bi-2212 crystals. The solid lines show contours of constant T_c values.[1] The dashed line with triangles shows the pO_2-T path followed during cooling of the samples to 25°C.

Fig. 2. Critical current density vs. magnetic field curve at 4 K for a controlled pO_2 cooled Bi-2212/Ag tape. The self field I_c is 93 A.

Bi-2212 THICK FILM ISOTHERMAL MELT PROCESSING

An alternative processing scheme has been developed for producing Bi-2212 thick films on Ag foils at temperatures 100°C lower than for conventional processes.[2] In this process, the powders are first melted in a low partial pressure of oxygen (pO_2) after which the pO_2 is increased and solidification of the sample takes place. Isothermal melt processing is feasible because of the large decrease in the solidus temperature with the decrease of pO_2. (This same techniques has also been used in the processing of round wires of Bi-2212, where it has lead to improved high critical currents.[3]) It is possible to grow high quality films with few second phases and good transport properties at temperatures as low as 770°C. A series of samples was isothermally processed in 10% O_2/Ar from 760°C up to 860°C. There appear to be five distinct isothermal melt processing regions where different competing events shape the microstructure and superconducting characteristics of the films. Critical current density values are summarized in Fig. 3.



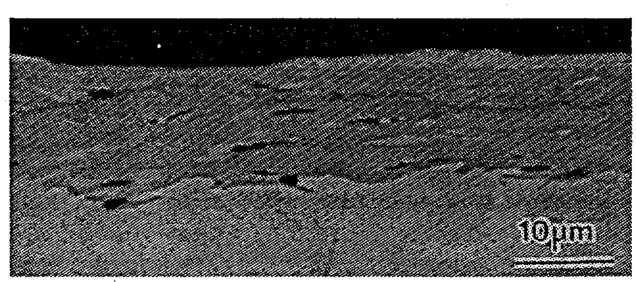


Fig. 3. J_c values at 4 K vs. processing temperature for isothermally melt processed tapes.

Fig. 4. Backscattered scanning electron microscope image of a film isothermally melt processed at 780°C.

In the first region below approximately 770°C, the main factor affecting the film is the viscosity of the melt. A rippled melt surface leads to a non-planar surface and disruptions in the laminar microstructure of the oxidized films. This same morphology has also been reported for thick films processed conventionally in air. In the second region between 770°C and 790°C, the melt in Ar forms a uniform layer across the substrate, yet the temperature is not high enough to allow for the formation of large CaO grains near the surface of the film. CaO can be found in the melt of a nominal Bi-2212 composition in an inert atmosphere below approximately 900°C, and it can act as a nucleation site for the formation of large alkaline-earth cuprates. However, in the temperature range of 770°C to 790°C, the formation of large CaO particles in the melt can be controlled and minimized resulting in highly textured films with excellent phase purity. A cross section of such a film is shown in Fig. 4. In the third region between 790°C and 840°C, large needles of the 1:1 phase were found to form due to CaO segregation. Large amounts of Bi-2201 were also found mixed in with the Bi-2212 phase. By the lever rule, this also results in the formation of a more Bi rich phase, Bi-2201. Both these phases act as a barrier to current flow, and the 1:1 phase also disrupts the texture. In the fourth region from 840°C to 850°C, the growth of the 1:1 phase still affects the properties of the film. However, the detrimental effect of CaO segregation is tempered by Bi loss during melting and solid state diffusion at these higher processing temperatures resulting in a local microstructure that is relatively phase pure Bi-2212, thus relatively high J_c values were also found. In the fifth region at 860°C, J_c decreases again, and two possible causes are immediately apparent. The microstructure has dramatically coarsened and the grain sizes of the two primary phases, 1:1 and Bi-2212, have increased substantially. The 1:1 needles form a network and coarsen to widths comparable to the sample thickness, and the Bi-2212 exhibits significant basal plane cracking.

In summary, a novel processing technique has been developed for high quality, highly textured Bi-2212 thick films on Ag tape. The isothermal melt process allows these films to be made at much lower temperatures than with conventional melt processing in air. The best films were achieved at 780°C and contained only very small quantities of Bi-2201 and alkaline earth cuprates, and these latter phases were not found as large needles. The best J_c result for films processed at 780°C was 120 kA/cm^2 (I_c = 145 A) at 4 K and self field. This represents a powerful processing technique for achieving high quality thick films at reduced processing temperatures.

Bi-2212/Ag AND Bi-2223/Ag TAPES WITH Ag RIBBONS

The addition of large Ag particles to the superconductive core of oxide powder in tube tapes results in better geometric uniformity during mechanical deformation thus resulting in thinner cores with concomitant better transport properties than can usually be achieved without resorting to multifilamentary conductors.[4] 20 wt% of 99.99% pure Ag powder with an average size of 38 μm was added to Bi-2212 powder from Seattle Specialty Ceramics, which had an average size 4 μm, and thoroughly mixed. The powders were hand packed into a Ag tube, sealed, drawn to 2 mm diam, then rolled to various thicknesses. Tapes were heated in air to 880°C at 10°C/h, held for 20 minutes, cooled to 845°C at 10°C/h, from 845°C to 835°C over 24 h, and furnace cooled to room temperature. The Ag particles remained spherical during wire drawing due to the low (45%) packing density of the superconductor powder, but they were deformed into long, thin ribbons during the rolling process. Ag powders with particle sizes from 3 to 200 μm were investigated; a size of 38 μm resulted in the best core uniformity and Ag deformation.

Figure 5 shows the longitudinal cross sections of as-rolled Bi-2212/Ag tapes containing Ag ribbons and a reference sample. The Ag particles are deformed into ribbons in the longitudinal direction. These Ag ribbons not only improve the mechanical properties during deformation by reducing the sausaging and cracking, etc., that are observed in the tape without Ag ribbons, but also provide extra superconductor/Ag interfaces, which is believed to benefit the Bi-2212 phase formation and grain alignment, and this is supported by the results. Because of the presence of Ag ribbons in the superconductor core, the tape could be rolled to as thin as 51 μm without necking, sausaging, or cracking. The Ag ribbons are spheroidized at the end of the heat treatment. This phenomenon results from the diffusion of silver and occurs to minimize surface area. The ribbons remain after the melting of the Bi-2212 and consequent cooling to 845°C with some thickening but spheroidize during the cooling from 845°C to 835°C. Figure 6 shows the *critical current density* J_c *at 4 K and self field as a function of superconductor core thickness.* As the core thickness decreases to about 23 μm, J_c exceeds 10^5 A/cm^2, about 60% higher than that of a tape without the Ag ribbons but processed identically.

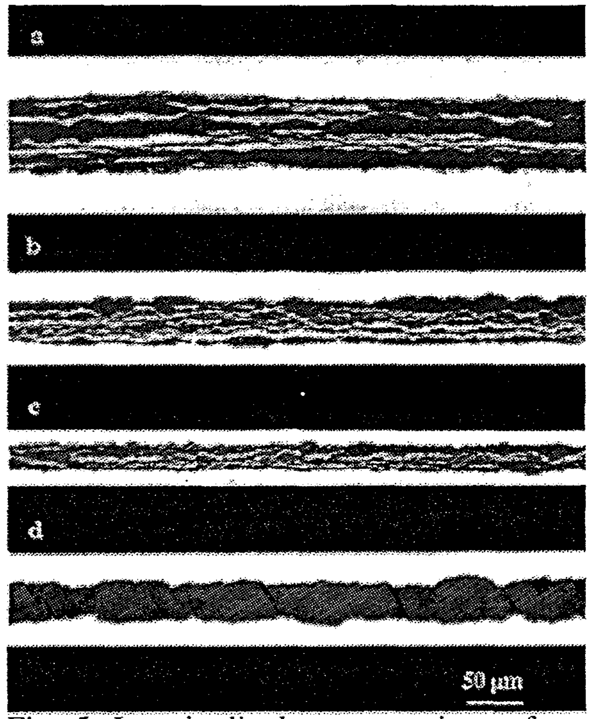


Fig. 5. Longitudinal cross sections of as-rolled tapes containing Ag ribbons with core thicknesses of (a) 70 μm, (b) 40 μm, and (c) 23 μm; (d) has no ribbons and shows significantly more cracking and sausaging.

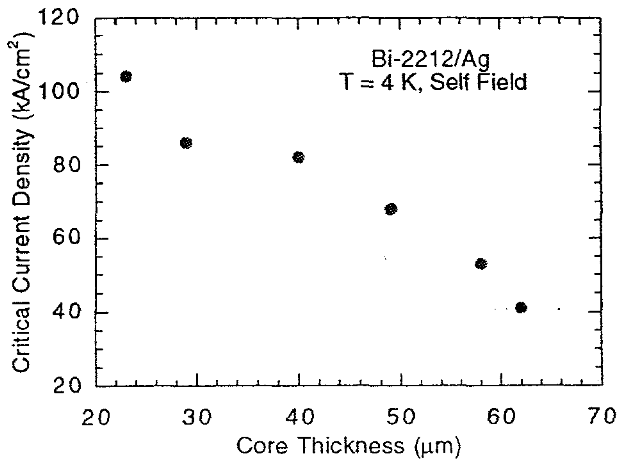


Fig. 6. Critical current density J_c *vs.* superconductor core thickness at 4 K, self field.

In summary, for the optimum 38 μm particle size, Ag added to Bi-2212 powder for OPIT tape fabrication stretches into long, thin ribbons during rolling. This ceramic/metal composite has excellent properties during deformation. Tapes were rolled as thin as 51 μm with a 23 μm core with no necking, sausaging, or cracking in the superconductor core. The Ag ribbons also provide additional Ag/HTS interfaces to help Bi-2212 phase formation and grain alignment. Improved critical current densities were obtained at both 4 K and 26.2 K. Similar performance improvements have also been found with large Ag particles added to Bi-2223 powder.[5]

DEFORMATION PROCESSING

The attainment of homogeneous structures in HTS composite tapes is central to their critical current density (J_c) properties. This requirement is often coupled with the desire to obtain thin cores for enhanced reaction and good J_c-bending strain characteristics. The primary deterrent to meeting these goals is the effect of the mechanical mismatch between the relatively hard HTS core and the compliant Ag cladding during rolling. Attempts have been made to rectify this situation by experimentation with stronger Ag alloy sheaths. However, chemical compatibility requirements have restricted the range of materials under consideration, and this has limited the understanding of the requirements necessary to obtain good core uniformity. To address this issue, a 3 factor experimental design was adopted with reductions of 25% and 5% per pass; relative core thicknesses of 0.2 and 0.6, and 3 sheath materials resulting in different yield strengths and work-hardening conditions (Yield Strengths: Al - 180 MPa, Ag - 300 MPa, Cu-3Si - 480 MPa). The powder used for these OPIT tapes is a Bi-2223 partially sintered precursor, which was hand packed into a Ag tube. The tube was drawn to wire through a series of low-angle dies, and rolling reductions were performed on a 4-high mill with 38 mm diam rolls. The generation of instabilities during the deformation of composite materials can be described as a bifurcation from a state of homogeneous strain to non-uniform strain. Depending on the stress state during deformation, this heterogeneous strain may manifest itself as a singular neck, as in uniaxial tension, or as periodic perturbations, such as those encountered from rolling. Periodic instabilities may exhibit two modes, depending on the relative strengths of the core and cladding, as shown in Fig. 7.

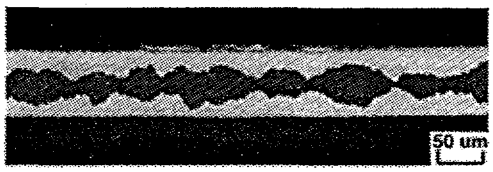


Fig. 7a. Symmetric (necking) mode is a result of a strong core and weak sheath (Ag).

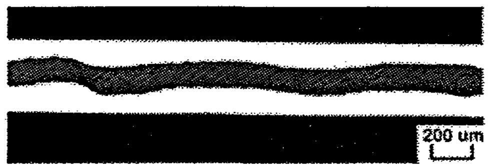


Fig. 7b. Anti-symmetric (undulating) mode generated with a weak core and strong sheath (Cu-3Si).

In summary, increased rolling reduction-per-pass is strongly correlated with non-uniform straining of HTS tapes in silver- and aluminum-clad systems. The effect of increased reduction-per-pass is to accelerate powder compaction, thereby exacerbating the mechanical mismatch between sheath and cladding. A strong sheath alone does not preclude the possibility of developing instabilities (Fig. 7b). However, stronger sheaths appear to reduce the sensitivity of bifurcation to reduction-per-pass. Bifurcation modeling provides insight for the control of bifurcation initiation.[6] As predicted by modeling, increasing the sheath work-hardening rate appears to diminish the tendency toward non-uniformity with continued reductions.

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