PHASE DEVELOPMENT IN PARTIAL-MELT PROCESSING OF SILVER-CLAD Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_2$O$_x$ TAPES*

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Abstract

Ag–clad Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_{2}$O$_x$ tapes were fabricated by the powder–in–tube method and heated in air to maximum temperatures of 880–895°C. The tapes were characterized by differential thermal analysis, scanning electron microscopy, energy–dispersive X–ray analysis, and X–ray diffraction. Microstructures of tapes that were heated at 885–895°C were similar, and, at a given temperature, remained stable for up to 1.0 h, which was the longest time used. The most significant microstructural features in specimens quenched from the melt were voids of up to ~400 μm in diameter. CuO was a minor phase in the melt, but grew significantly upon cooling to become the major nonsuperconducting phase when solidification was complete.
Introduction

Heat treatment of Bi$_2$Sr$_2$CaCu$_2$O$_x$ (Bi–2212) conductors always involves partial melting (1). The Bi–2212 compound is a solid solution and many other compounds are in equilibrium with it during heating (1-10). Although there is minor disagreement in the literature, most phase diagrams indicate that the Bi$_2$Sr$_2$CaCu$_2$O$_x$ composition does not exist within the single–phase region of the superconductor and that the actual compound tends to be rich in Bi and deficient in Sr (1-14). A reasonable average composition for the centroid of the single–phase field is approximately Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_2$O$_x$ (2-10).

The Bi$_2$Sr$_2$CaCu$_2$O$_x$ composition has been used in most work on Bi–2212 conductor development. In particular, microstructural evolution during partial–melt processing has been studied extensively (15-21). Bi$_2$Sr$_2$CaCu$_2$O$_x$ has been shown to produce excellent final microstructures consisting of large, well–textured grains of Bi–2212, often with minor concentrations of alkaline–earth cuprates such as (Sr,Ca)CuO$_2$ (1/1), (Sr,Ca)$_2$CuO$_3$ (2/1), or (Sr,Y,Ca)$_{14}$Cu$_{24}$O$_{38}$ (14/24). Critical current densities > 5 x 10$^5$ A/cm$^2$ at 4.2 K have been reported for partial–melt–processed Ag–clad Bi–2212 conductors (1). It has also been reported, however, that the maximum heat–treatment temperature must be controlled to within a few degrees centigrade to produce optimal superconducting properties (21).

The work reported here was undertaken to examine microstructural development during partial melting, and to determine whether Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_2$O$_x$ yields good microstructures. Our previous work focused on a Sr–deficient composition, Bi$_2$Sr$_{1.7}$Ca$_1$Cu$_2$O$_x$ (22-25). In contrast to Bi$_2$Sr$_2$CaCu$_2$O$_x$, for Bi$_2$Sr$_{1.7}$Ca$_1$Cu$_2$O$_x$ heated in air, the 14/24 phase was highly stable and solid Cu–free phases were not observed (23). Although phase diagrams can offer guidance to what phases will be present in partial–melt–processed Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_2$O$_x$, their size, distribution, and range of conditions over which they will persist will be determined primarily by kinetics. Furthermore, for real Bi–2212 conductors, Ag is nearly always present as a sheath or substrate, and its presence will alter phase development. We have therefore fabricated Ag–clad tapes and heated them over a range of temperatures and times. Specimens were quenched from various points in the heat–treatment cycle and their microstructures were examined.

Experimental Details

Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_2$O$_x$ powder was prepared from reagent–grade Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$, and Cu$_2$(OH)$_2$CO$_3$. A 120–g batch was prepared, placed in a high–density polyethylene jar and ball milled for 16 h with ZrO$_2$ grinding media in isopropyl alcohol. The powder mixture was then dried while being stirred, screened through a 30–mesh sieve (26), placed in a shallow Al$_2$O$_3$ crucible, and heated as follows: in flowing high–purity O$_2$ at a total pressure of 5 x 10$^5$ Pa, 120°C/h to 650°C, held 1 h, and heated 10°C/h to 750°C, held 6 h; switched to dry, CO$_2$–free air and heated at 120°C/h to 875°C, held 0.1 h, cooled to 840°C at 120°C/h, held for 60 h, and cooled at =100°C/h to room temperature. The partial–vacuum heating was used to minimize retention of carbon in the powder (26-30).

X–ray diffraction with Cu K$\alpha$ radiation indicated that the powder was nearly phase–pure Bi–2212 (Fig. 1); however, trace impurities, especially Ca–Cu
oxides, are difficult to detect with X-rays (31). Differential thermal analysis, with Al$_2$O$_3$ as the standard and a heating rate of 300°C/h, revealed an onset of significant melting at $\approx$868°C (Fig. 2). A change of inflection of the primary endotherm suggested that the Bi–2212 phase probably melts in air closer to 875°C and that the lower onset temperature was associated with minor second phases (32).

Figure 1 – Powder X-ray diffraction pattern of as-synthesized Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_2$O$_x$.

Figure 2 – Results of differential thermal analysis in air of as-synthesized Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_2$O$_x$ powder.
The powder was crushed with an agate mortar and pestle, loaded into 99.9% Ag tubes, 6.35 mm in outer diameter and 4.35 mm in inner diameter, and processed into flat tapes. The combination of drawing and cold-rolling that was employed has been described (22-25). The final tapes were =200 μm thick.

All of the tapes were heat treated in dry, CO₂–free air. For many tapes, however, the initial heating through 750°C occurred in flowing O₂ at a total pressure of 5 x 10² Pa. The schedule is shown in Fig. 3. The segments at 740 and 835°C, which were designed to remove C from the core (28,29), were included for most, but not all, tapes. We found that the 835°C hold was sufficient to bring the C content of the core to =400 ppm. All of the specimens were quenched either from T₁ or from 855°C following heating at T₁. One tape was rapidly quenched in oil; the others were air–quenched.

Each tape was polished, coated with C, and examined by scanning electron microscopy (SEM); energy dispersive X–ray analysis was used to obtain chemical compositions during the SEM. Several tapes were also examined by X–ray diffraction.

Results and Discussion

In examining the quenched microstructures, our first consideration was the composition, size, and volume fraction of the crystalline phases present above the peritectic melting temperature. For a composition of Bi₂Sr₂CaCu₂Oₓ, the primary phases are 1/1 and a Cu–free phase [1,17]. For tapes processed in air, the 1/1 phase can be quite large, and thus difficult to consume during solidification of the Bi–2212 phase. We hoped to limit 1/1 formation through the presence of the added Bi in the Bi₂.1₅Sr₁.₈₅Ca₁.₀₂Cu₂Oₓ.

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Figure 3 – Heat–treatment schedule for Ag–clad Bi–2212 tapes; 880 ≤ T₁ ≤ 895 and 0 h ≤ t₁ ≤ 0.5 h.
As shown in Fig. 4, the tape microstructures were different from those reported previously. First, and foremost, the dominant features were voids, not crystalline phases. Second, the 2/1 phase was the dominant alkaline-earth cuprate, although the 1/1 phase was also present. Third, the 2/1 phase was thin and acicular, with maximum lengths up to \(=1\) mm. Fourth, small CuO particles were present in dilute concentrations. Compared with our previous work, the alkaline-earth cuprates are vastly different. For Bi\(_2\)Sr\(_{1.7}\)CaCu\(_2\)O\(_x\), the dominant phase was acicular 14/24 and its maximum size could reach >3 mm \([22,23]\). The 2/1 phase in the current tapes was much smaller and its volume fraction lower. Tapes were held above the partial-melt temperature from 0 to 1.0 h. The volume fraction and size of the 2/1 phase were, within experimental error, constant with time. In this respect, the new Bi-rich composition must be judged a success. The alkaline-earth cuprates were relatively small and scarce. There was a slight trend for higher partial-melt temperatures to produce smaller 2/1 phases.

The question of the large voids remains to be addressed. It was found that, in tapes for which no premelting anneals were conducted, and thus the C concentration was high (probably >1000 ppm), the voids were larger and more numerous (Fig. 5). It was also found that increasing the partial-melt temperature from 885 to 890°C decreased the size and areal fraction of the voids (Fig. 6). Heating at higher temperatures is likely to drive off more C, and thus the trend of smaller voids with less C obtains. However, the total C concentrations of the tapes shown in Figs. 4 and 6, for which anneals were conducted to remove C, were all <400 ppm. For a similar C concentration, the Bi\(_2\)Sr\(_{1.7}\)CaCu\(_2\)O\(_x\) composition that we used in earlier studies did not produce such voids, nor does the conventional Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_x\) composition \([1,15-17,22-26]\). Furthermore, the tapes were only \(=4\) cm long and the ends were open, so evolved gas should have had a chance to escape. Void formation was doubtless caused by internal gas pressure. Why the voids were so large and numerous only in the Bi\(_{2.15}\)Sr\(_{1.83}\)Ca\(_{1.02}\)Cu\(_2\)O\(_x\) tapes is not clear; the phenomenon may be related to the presence of extra Bi in the melt. Perhaps the heavier liquid phase entrapped gas bubbles rather than allowing them to pass out the ends of the tape or through the sheath.

Figure 4 – SEM photomicrograph of Ag-clad Bi\(_{2.15}\)Sr\(_{1.83}\)Ca\(_{1.02}\)Cu\(_2\)O\(_x\) tape heated for 0.3 h at 885°C (polished parallel to the plane of the tape); (a) large dark regions are voids, (b) gray needles are 2/1 phase, (c) smaller more equiaxed gray regions are 1/1 phase, and (d) dark-gray particles are CuO.
Chemical analysis revealed that the core of each tape contained a significant concentration of Ag. During cooling, the Ag coalesced into large particles (Fig. 7). Although all of the Bi-2212 compositions dissolve some Ag from the sheath during heat treatment [32], we are unaware of previous reports of such large Ag regions. We also observed that growth of the Bi-2212 phase after melting was accompanied by reduction in the size and fraction of the 2/1 and 1/1 phases and the large voids shown in Fig. 4 (although, in a few places, voids up to =200 μm in diameter remained) and by an increase in the size and fraction of CuO (Fig. 7).

Several general statements can be made from the quench studies. Unlike the partial melt of Bi$_2$Sr$_2$CaCu$_2$O$_x$, for which the 1/1 phase + a Cu-free phase dominate, or the partial melt of Bi$_2$Sr$_{1.7}$CaCu$_2$O$_x$, for which the 14/24 phase dominates, partial melting of Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_2$O$_x$ produced primarily 2/1, minor 1/1 and CuO, and no Cu-free crystalline phases. Significant Ag was dissolved from the sheath during melting. Cooling to 855°C and holding for 3 h resulted in growth of both the Bi-2212 phase and CuO, and in segregation of the dissolved Ag. No firm answer was found to the question of the effect of maximum heat treatment temperature on microstructural development.

Microstructures were dominated by features not generally reported: large voids, dissolved Ag, and large CuO particles, not by alkaline-earth cuprates.

The results reported here can be extended. It may be that other heat-treatment schedules or heat-treatment atmospheres may prove to be better suited to processing the Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_2$O$_x$ composition [1,33]. To date, however, the prospects for the utility of Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_2$O$_x$ do not appear bright. As a benefit, formation of alkaline-earth cuprates during melting is somewhat restricted by the extra Bi. Several drawbacks are, however, apparent. The composition appears to be susceptible to void formation and aggressive toward Ag sheaths. CuO growth during solidification of the Bi-

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**Figure 5** - Relationship of (a) volume fraction ($V_f$) and (b) diameter of voids to time of heating in air at 890°C for tapes polished parallel to the plane: with a preanneal to remove C (filled triangles) and without such an anneal (open triangles).
2212 phase after partial melting may be especially deleterious. A phase diagram for the Bi–2212 system at 850°C from Majewski [10] indicates that the compatibility triangle for Bi–rich, Sr–deficient compositions is bounded by Bi–2212, a Bi–rich liquid, and CuO. The liquid would allow rapid growth of CuO during cooling [34,35], as was observed. Although it may be possible to cool rapidly to a temperature lower than 850°C, and thus minimize CuO growth, such deeper cooling will also slow Bi–2212 growth and promote nucleation of more Bi–2212 grains. The resultant smaller grain size would reduce transport $J_c$.

Figure 6 – Relationship of (a) volume fraction ($V_f$) and (b) diameter of voids to time of heating in air at 885°C (circles), 887.5°C (diamonds), and 890°C (triangles).

Figure 7 – SEM photomicrograph of Ag–clad Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_{2}$O$_{x}$ tape heated for 0.2 h at 885°C and cooled to 855°C and held for 3 h (polished parallel to the plane of the tape); large dark–gray particles are CuO and gray circular regions are Ag.
Conclusions

Ag-clad Bi$_{2.15}$Sr$_{1.83}$Ca$_{1.02}$Cu$_2$O$_x$ tapes were heat treated in air to maximum temperatures of 880–895°C. Microstructures of tapes that were heated to 885–895°C were similar. The dominant features were large, nearly equiaxed voids and the (Sr,Ca)$_2$CuO$_3$ phase. (Sr,Ca)CuO$_2$ and CuO were minor phases in the melt, but the CuO grew significantly upon cooling to become the major nonsuperconducting phase when solidification was complete. A published phase diagram [10] indicates that it will be difficult to restrict CuO growth in Bi–2212 compositions that are Bi–rich and Sr–deficient.

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References


