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 $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ Superconductors*

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Thermomechanical Processing of Ag-Clad

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Abstract

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212) powders were synthesized by solid-state reaction, loaded into Ag tubes, and processed into tapes by various combinations of drawing, rolling, and heat treatment. Critical current densities at 4.2 K of greater than 10^5 A/cm^2 were achieved from microstructures consisting of large, highly textured 2212 grains. Optimal microstructures were produced by specific mechanical-working conditions and heat-treatment schedules that incorporated solid-state and partial-melt sintering. The relationships between processing, microstructure, and critical current density will be discussed.

Introduction

It has been shown that Ag-sheathed $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212) tapes fabricated by the powder-in-tube method have high current-carrying capability at 4.2–25 K. Tenbrink et al. (1) used a partial-melting process for 2212 wire fabrication and produced a critical current density (J_c) at 4.2 K exceeding 10^4 A/cm^2 to fields of 25 T. Kase et al. (2) determined that large, highly c-axis-aligned grains were developed by the use of partial-melt processing, which consisted of melting at $\approx 890^\circ\text{C}$, followed by prolonged annealing at $\approx 870^\circ\text{C}$. However, because of characteristics of the peritectic reaction, nonsuperconducting phases such as alkaline-earth cuprates, alkaline-earth bismuthates, CaO, and CuO also formed. The alkaline-earth cuprates could grow quite large during cooling. These secondary phases disturb the local 2212 alignment and obstruct the current path, consequently decreasing J_c .

The optimum maximum temperature of the partial-melt process is reported to be $880\text{--}920^\circ\text{C}$, depending on the stoichiometry of the 2212 and the atmosphere. (1,2) However, the subsequent optimal annealing temperature and time are not so clearly defined. The 2212 phase will crystallize quickly from Bi-Sr-Ca-Cu-O glasses over a broad range of temperature and time. (3) This implies that the annealing conditions for 2212 formation may not be critical. The purpose of this work was to clarify the relation between heat treatment and microstructure for 2212 tapes. The growth kinetics of the secondary phases and the effects of rolling conditions on J_c were also studied.

Experimental Details

The Ag-clad tapes had the nominal cation molar content 2.0:1.7:1.0:2.0 (Bi:Sr:Ca:Cu). The starting powder was made by solid-state reaction of oxides and carbonates. (4) The phases after calcination were 2212 and trace amounts of $\text{Bi}_2\text{Sr}_2\text{CuO}_x$ (2201) and CaO. The reacted powder was packed into an Ag tube and drawn and rolled to a tape 0.1–0.2 mm thick and $\approx 3 \text{ mm}$ wide.

A series of quench experiments was conducted to monitor the kinetics of nucleation and growth of the superconducting and secondary phases. During heating, specimens were quenched from 850, 860, 870, 880 and 890°C . Two more specimens were quenched after 0.1 and 0.5 h holds at 890°C . A 10°C/h cooling rate was used to cool the tapes from 890°C to 880, 870, 865, 860 and 855°C . Tapes were quenched after 1 and 3 h holds at 870, 865, 860 and 855°C . Rolled tapes (length = 5 cm, width = 0.4 cm, thickness = 0.2 mm) were heated to the selected temperatures and then quenched into ice water. The distance between the quench medium and the outlet of the furnace was small to minimize the possibility of air quenching. Complete partial-melt heat treatments were also performed (Table 1). After partial-melt treatment, some tapes were rolled to $\approx 0.15 \text{ mm}$ with various reductions per pass, and a final annealing treatment was conducted at 840°C in air for 100 h.

Onsets of significant melting were determined by differential thermal analysis (DTA) in air. Phase identification and grain alignment of the tapes were determined by X-ray diffraction

(XRD) and scanning electron microscopy (SEM) with energy dispersive analysis of X-rays (EDS). Degree of c-axis alignment was defined as the ratio of the intensity of the (001) to the (117) peak. Current-voltage characteristics for Ag-clad tapes were measured by the conventional d.c. four-probe method at 4.2 K; J_c was defined by a 1 $\mu\text{V}/\text{cm}$ criterion.

Table 1. Partial-Melt Treatment of 2212 Tapes

Schedules	Partial-melt Temp ($^{\circ}\text{C}$)	Cooling Rate ($^{\circ}\text{C}/\text{h}$)	Holding Temp ($^{\circ}\text{C}$)	Holding Time (h)
1	890	10	870	3
2	890	10	865	3
3	890	10	860	3
4	890	10	855	3

Results

Figure 1 shows the DTA curve of a typical Ag-sheathed 2212 tape. The endotherm at $\approx 884^{\circ}\text{C}$ was due to incongruent melting of the 2212 phase. During cooling, an exotherm was observed between 865 and 850°C . This peak, as will be discussed later, was due to solidification of 2212 phase. The delay in solidification relative to melting resulted because nucleation required undercooling to overcome the nucleation energy barrier to form critical nuclei.

Figure 2a shows the XRD data for tapes quenched from five different temperatures during cooling. No 2212 or 2201 formed from 880 to 865°C . Small peaks of $(\text{Sr,Ca})_2\text{CuO}_3$ (2.1) and $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_x$ (14/24) were detected in this temperature range. (5) At 860°C , the 2212 phase began to form; its intensity increased substantially at 855°C . No significant texturing of 2212 grains was observed. The 2.1 and 14/24 phases were also detected at 860 and 855°C . XRD data of tapes quenched after 1 h at various temperatures are shown in Fig. 2b. After 1 h at 870°C , no 2212 or 2201 was observed; 2212 formed at 865°C , with a small amount of favorable texture. The texture was strongly developed after 1 h at 860°C , but was less strong after holding at 855°C . Figure 2c shows the XRD data of tapes quenched after 3 h at temperature. The results were similar to those shown in Fig. 2b. Again, the strongest c-axis texture was developed at $\approx 860^{\circ}\text{C}$ (Table 2).

Figure 3 shows SEM micrographs for various quenched tapes. Small amounts of needle-like alkaline-earth cuprate phases, 14/24 by EDS, started to form at 860°C (Fig. 3a); average size was $\approx 100 \mu\text{m}$ long and $\approx 10\text{--}20 \mu\text{m}$ wide. As temperature increased to 880°C , the secondary phases grew rapidly to $\approx 300\text{--}400 \mu\text{m}$ in length, and the volume fraction increased (Fig. 3b). Above 880°C , the 14/24 phase decomposed and the 2.1 phase formed. After 0.5 h at 890°C , the temperature was decreased at $10^{\circ}\text{C}/\text{h}$ to different temperatures. Figure 3c shows the microstructure of a tape quenched from 880°C during cooling. The size of the secondary phase remained about the same as that at 890°C ; however, the volume fraction increased.

Figure 1. DTA Curve for Ag-Sheathed 2212 Tape

Table 2. The XRD Peak Ratio of (0010) to (117) of Quenched Tapes at Various Holding Temperatures and Times

	0 h	1 h	3 h
870°C	0	0	0
865°C	0	1.28	1.03
860°C	1.36	1.97	2.03
855°C	1.17	1.45	1.57

Substantial coarsening of the secondary phases took place during the cooling from 880°C to 870°C. In tapes quenched at 870°C, secondary phase 800–1000 μm long and 50–100 μm wide were observed (Fig. 3d). EDS analysis indicated that these phases were 14/24. Smaller 2.1 phases (100–200 μm long, 10–20 μm wide) were also observed. Substantial growth of the platelike phases was observed after holding 3 h at 870°C (Fig. 3e). Large 14/24 phases were also observed in the tapes quenched from 865 and 855°C (Figure 3f-h). In particular, remarkable coarsening occurred after 3 h at 865°C. However, no coarsening occurred after 3 h at 855°C. Little coarsening of the 2.1 occurred for any cooling schedule. The volume fractions of the 14/24 and 2.1 as a function of quenching temperature during heating and cooling are shown in Figs. 4 and 5. The volume fraction of 14/24 phase as a function of holding time at various temperatures is shown in Fig. 6. Substantial increases occurred with holding at 870 and 865°C, but not at 860°C and 855°C.

SEM micrographs for tapes after full partial-melt heat treatments are shown in Fig. 7. The dominant phase was 2212, but small amounts of 2201 were always observed. Figure 7a shows a tape annealed 3 h at 865°C. Well-aligned 2212 grains developed near the Ag interface, producing a structure favorable for passage of electrical current.

(a)

(b)

(c)

Figure 2. XRD for the Tapes Quenched After (a) 0 h, (b) 1 h, (c) 3 h Holds at Various Temperatures, with a Cooling Rate of 10°C/h from 890°C

Figure 3. Microstructure of Tapes Quenched from Various Holding Temperatures and Times on Heating and Cooling

Figure 4. Volume Fraction of Secondary Phases as a Function of Temperature upon Heating

Figure 5. Volume Fraction of Secondary Phases as a Function of Temperature upon Cooling

Figure 6. Volume Fraction of 14/24 as a Function of Annealing Time at Temperature

However, some 2212 grains adjacent to secondary phases grew along the interface, and thus the growth direction was not parallel to the rolling direction. In addition, some 2212 grains stopped growing when their growth fronts were obstructed by secondary phase. Presence of large second phases reduced the extent of favorable texture. The microstructure of tapes annealed at 860°C is shown in Fig. 7b. Well-aligned grains were present throughout the entire oxide core. Some 2201 (lighter gray) grains were embedded between the 2212 (darker gray) grains. The microstructure of tapes annealed 3 h at 855°C is shown in Fig. 7c. The desired well-aligned grain structure was only present near the Ag interface. Randomly oriented grains were present throughout the central zone of the oxide core. In addition, some 2212 grains penetrated into Ag and disrupted the well-textured structure at the Ag interface.

The J_c values for the tapes after partial-melting treatment, but before final rolling and heat treatment at 840°C, are shown in Fig. 8. Highest J_c values were produced by annealing at 860–865°C. A tape that was held 3 h at 860°C in partial-melt step and final annealed 100 h at 840°C yielded the highest J_c at 4.2 K, 1.5×10^5 A/cm². The highest J_c value was produced by rolling with 10% reduction per pass; larger reductions per pass decreased J_c values about 50%. (4) The effect of annealing time at 840°C on J_c is shown in Fig. 9. In this processing, at least ≈ 100 h was needed to produce a high- J_c tape.

Discussion

The broad exotherm on the DTA curve ranged between 865 and 850°C. Maximum heat was released from this system at $\approx 857^\circ\text{C}$. If the heat of this exotherm is due to latent heat released by solidification of 2212, this curve indicates that the nucleation process of 2212 started at $\approx 865^\circ\text{C}$ and the maximum number of nuclei formed at $\approx 857^\circ\text{C}$. XRD analysis of tapes quenched during cooling shows that no 2212 phase forms until 860°C during continuous cooling. 2212 peaks were observed after 1 h at 865°C. No 2212 formed at 870°C. These results confirm that the DTA exotherm was due to solidification 2212. XRD data for the tapes quenched after 1 h at various temperatures during cooling indicate that better texture of 2212 was obtained at 860°C than at 855°C. In addition, the grains of the tapes annealed 3 h at 865°C and 860°C exhibited better alignment than in tapes annealed at 855°C. High J_c was produced by heat treatment at 865 and 860°C. The XRD, SEM, and J_c results indicate that a tape with better microstructure, primarily maximum c-axis alignment, and better electrical properties can be produced by cooling from 890°C to 860–865°C, holding there for about 3 h, and cooling to room temperature. Generally speaking, low nucleation rates and high growth rates during phase transformations or solidification are required for a large-grained microstructure. The desired structure for good electrical properties of high- T_c superconductor is one in which the grains are large and aligned parallel with the direction of current flow. Kase et al. (2) found that 2212 grains nucleated easily and grew rapidly along Ag interfaces. A 20- μm -thick layer of well-aligned 2212 grains parallel with Ag interface was formed at the interface during cooling from 890°C to 870°C. It is believed that this thin well-aligned grain layer is the major region of current flow. (2) The thicker this layer, the higher J_c . Therefore, the effort is to find a proper partial-melt schedule to increase the thickness of this well-aligned

(a)

(b)

(c)

(d)

Figure 7. SEM Microstructure of Tapes Partially Melted with (a) Schedule 1, (b) Schedule 2, (c) Schedule 3, and (d) Schedule 4, as Listed in Table 1

Figure 8. J_c at 4.2 K for Tapes Heat Treated by Schedules Listed in Table 1

Figure 9. Relationship between J_c and Sintering Time at 840°C in Air

grain structure near the Ag interface. Ag, essentially acting as a mold wall in the solidification process, is a favorable site for heterogeneous nucleation of 2212. However, due to the secondary phase present in the BSCCO oxide core, 2212 can also nucleate on these particles easily and, because of the random distribution of these secondary phase, the growth directions of the 2212 are also random.

The grain structure produced during partial-melt processing is determined by competition between growth of 2212 in two regions: first, is the region near the Ag interface where the 2212 grains are well-aligned, and second is the region near the center of the oxide core where the 2212 grains may grow along interfaces with secondary phases. It has been found that addition of Ag to 2212 can drop the melting point by $\approx 15^\circ\text{C}$. (4) Fang et al. (6) showed that diffusivity of Ag is high at high temperature. It is possible that there exists a layer of the core near the Ag interface in which the melting point is lowered because of the presence of Ag. As

a result, more liquid may be present in this Ag-rich layer than in areas with less Ag. This liquid-rich zone near the Ag interface may promote growth of 2212 after it has nucleated on the Ag. In the partial-melt process used here, 860–865°C is good for the desired grain structure, because of a low rate of nucleation and because of high growth rates due to the presence of liquid. However, coarsening of secondary phases takes place at $\approx 865^\circ\text{C}$ and higher temperatures. These coarse secondary phases have a deleterious effect on the overall alignment of 2212. Therefore, the holding temperature following partial melting should be at a temperature below that favored for coarsening of secondary phase. At 855°C, more nuclei are formed in the oxide and the thickness of the liquid-rich layer may be less than that at high temperature. As a result, thin layers of well-aligned grain structure near the Ag interface and random structures at the center are produced.

The highest J_c value after the partial-melting process was $\approx 2 \times 10^4 \text{ A/cm}^2$, which is below the value needed for most practical applications. The low J_c may be attributed to several reasons. First, due to the retrograde densification associated with anisotropic grain growth, the density of the oxide core decreased after partial melting. (7) Second, pores may have been generated during heating because of decomposition of residual carbonates or hydroxides (8), or sudden evolution of oxygen upon decomposition of the 2212. (9) Further rolling redensified the core and enhanced c-axis alignment by mechanical action. Post annealing was employed to connect the grains and heal the small cracks that may have been generated during the second rolling. However, severe mechanical working may result in irreparable damage, such as large cracks and sausaging. SEM revealed that sausaging was most pronounced in tapes with high concentrations of secondary phases. It appears that gradual and limited mechanical working is favorable for high current capability.

Assessment

The partial-melting process substantially affects the final microstructure and J_c Ag-clad 2212 tapes. Parameters to be controlled in this process are: atmosphere, maximum temperature, holding time at temperature, and heating and cooling schedules. The structures of 2212 and the secondary phase vary with these parameters, and consequently, electrical properties vary as well. In the second rolling step, severe reduction may cause damage; moderate reduction can densify the core structure, without introducing serious damage to the core. However, due to the size of the secondary phase, the thickness after the second roll can be limited. A post annealing process is essential to heal the cracks which are generated during rolling and to join the superconducting grains.

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