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ABSTRACT

High critical currents have been obtained in Bi-Sr-Ca-Cu-O by the powder-in-tube approach. Owing to the inherent structural anisotropy of the Bi-based high- T_c superconducting materials, high- J_c is only obtained when the wires are subsequently rolled into rectangularly cross-sectioned tapes. Previously, intermediate annealing was employed to maintain ductility in the silver with a high temperature sintering just before the final rolling in order to form the high- T_c superconducting phase. Here, we report on the effects of hot-rolling at various temperatures for the final rolling of powder-in-tube BSCCO-2212 tapes. Hot-rolling was accomplished by pre-heating the rolls with infrared heaters and rolling the tapes directly from the furnace. The highest current densities were obtained by final hot-rolling the 2212 tapes at 420°C with the furnace temperature of 750°C, the highest temperature studied. Results showed the enhancement of J_c was due to the improvement of grain alignment as well as the reduction of the size and fraction of Bi-free phases during the final heat treatment. Furthermore, an analytical model of the hot-rolling process has been developed that illustrates the importance of pre-heating the tapes and heating the rolls.

INTRODUCTION

Ag-clad tapes of Bi-Sr-Ca-Cu-O superconductors show great promise for application as a conductor in very high magnetic fields. Owing to the large anisotropy of superconducting properties, strong crystallographic texture is required. The microstructure-property results confirmed the importance of a highly c -axis aligned microstructure for the critical current density. Much effort ¹⁻⁴ has focused on improving the grain alignment. Previously, Ag-clad tapes were prepared by cold-rolling, resulting in a highly textured microstructure near the oxide/Ag interface, and a weakly textured region in the middle of the oxide core. Large second-phase particles induced major disruptions of the local grain

alignment⁵. An early study showed that warm-rolling improved J_c of thick YBCO/Ag tapes⁶. In the present work, we report on the effects of hot-rolling on the microstructure and critical current density of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$. Results from an analytical model of the hot-rolling process are also reported.

EXPERIMENTAL

The Ag-clad tapes used for hot-rolling were prepared by the conventional powder-in-tube procedure¹, which includes packing the 2212 powder into silver tube, drawing the tube into wire by cold work, cold-rolling the wire into tape and a partial-melting heat treatment "intermediate heat treatment". Two powder stoichiometries were studied: $\text{Bi}_2\text{Sr}_{1.7}\text{CaCu}_2\text{O}$ (2212) and $\text{Bi}_2\text{Sr}_{1.7}\text{CaCu}_2\text{O}+1\text{wt}\%\text{Pt}$ (Pt-2212). The partial-melting schedule for 2212 tapes was: heat slowly to 800°C , then more slowly to 890°C , hold 20min, cool at $2^\circ\text{C}/\text{min}$ to 860°C and hold for 3hrs, then cool at $2^\circ\text{C}/\text{min}$ to room temperature; the schedule for Pt-2212 was: heat at $3^\circ\text{C}/\text{min}$ to 800°C then slowly heat to 884°C for 8min, cool at $20^\circ\text{C}/\text{hr}$ to 863°C for 3hrs then cool at $2^\circ\text{C}/\text{min}$ to room temperature. Hot-rolling was accomplished at varying temperatures on the partially-melted tapes by pre-heating the rolls with infrared heaters and rolling the tapes directly from a furnace (see Fig.1). Tapes were pre-heated for 10 minutes at varying temperatures in the furnace. The reduction per pass was less than 10%. After hot-rolling, samples were annealed at 840°C for 100hrs. Table 1 is the hot-rolling and heat treatment schedule. After each step, various types of microstructural analyses were performed on the tapes. The broad surface was polished and examined by optical microscopy. Scanning electron microscopy (SEM) using a Hitachi S-800 equipped with a Link energy dispersive spectrometer (EDX) was used to examine the longitudinal cross section and perform composition analysis. Polished longitudinal cross sections were etched with 2 parts 70% perchloric acid mixed with 98 parts 2-butoxyethanol for 60-70s.

Fig. 1. Schematic diagram of hot-rolling apparatus.

After each step of the process, phase analysis and qualitative grain alignment of the 2212/Ag tapes were determined by X-ray diffraction. Tapes were mounted on an Al sample holder and polished. $\text{CuK}\alpha$ radiation was used with a voltage of 42kV and the current of 25mA. The range of 2θ was $10-65^\circ$, and the relative degree of the grain alignment was determined by calculating the ratio of the intensity of the (0010) peak to that of the (117) peak.

Superconducting properties were measured in a Quantum Design DC superconducting quantum interference device (SQUID) after the final heat treatment, with the magnetic field roughly parallel to the *ab* plane. The critical temperature was measured while warming in a 50 Gauss magnetic field after zero-field cooling. Magnetic hysteresis was measured for magnetic fields ranging between $\pm 5.5T$ at 5K and 20K. Critical current densities $J_{cm}(H)$ have been extracted from the hysteresis loops using Bean's model⁷, $J_{cm} = 30\Delta M/d$, where ΔM is the difference between magnetization in increasing and decreasing fields and d is the width of the oxide core (2-4mm). Transport J_c was carried out by four-probe resistive method at 4.2K with zero field. To minimize mechanical strain² during handling and transport measurement, samples were mounted on a printed-circuit board. Electric field criterion of $1\mu V/cm$ was used for I_c determination.

Table 1. Schedule of hot-rolling for the 2212 and Pt-2212 tapes

No. Sample	Final Rolling		Ratio of Intensity (0010)/(117)	Final HT °C(hrs)	Ratio of Intensity (0010)/(117)	T _c (magnetic) K
	furnace(°C)	rolls(°C)				
A0 2212 ¹	NA	NA	24.2	NA		
A1 2212	25	25	48.1	840(100)	40.8	83
A2 2212	350	300	50.5	840(100)	42.0	85
A3 2212	750	370	49.0	840(100)	49.7	84
A4 2212	750	420	65.2	840(100)	65.3	83
A5 2212 ²	750	400		890(0.3),860(3)		80
B0 Pt-2212 ³	NA	NA	22.9	NA		
B1 Pt-2212	25	25	40.9	840(100)	40.0	82
B2 Pt-2212	350	300	43.4	840(100)	44.0	86
B3 Pt-2212	750	300	50.6	840(100)	46.0	84

¹2212 tape after the partial-melting.

²2212 tape, first cold-rolled to 0.3mm then hot-rolled to 0.196mm followed by partial-melting

³Pt-2212 tape after partial-melting.

RESULTS AND DISCUSSION

Fig. 2 shows the optical microstructure of sample A4, hot-rolled at 420°C after pre-heating at 750°C. After the partial-melting (intermediate heat treatment), some Bi-free phases were observed (a), and confirmed by the compositional analysis using EDX. The Bi-free phases, however, were crushed during the hot-rolling (b), and melted and renucleated in the final heat treatment. The recrystallized Bi-free phases are very fine compared with the large size of Bi-free phases after the partial-melting (a). Some holes were formed along the two sites of original large Bi-free phases due to the diffusion of atoms at high temperature. Similar phenomena were observed in the cold-rolled samples.

Better grain alignment with large grain size was obtained using hot-rolling as shown in Fig. 3 and Fig. 4. SEM showed a loose and randomly oriented microstructure was usually observed with the alignment along the interfaces of oxide/Ag in the sample after the partial-melting. Final cold-rolling caused the grains to align and the microstructure to become more dense, but some arbitrary-oriented grains still existed as shown in Fig. 3 (c) for 2212

Fig. 2. Optical micrographs for 2212 tapes as partially-melted and hot-rolled: (a) first cold-rolled, then partially-melted; (b) same as (a), then hot-rolled at 420 °C (furnace 750 °C); (c) same as (b), followed by 840 °C for 100hrs.

and Fig.4 (b) for Pt-2212. The local grain alignment was hampered by large second phases that appeared during the partial-melting process (see Fig. 3b). The microstructure of the longitudinal cross section for the sample A4 showed better grain alignment compared with the cold-rolled sample, which was confirmed by X-ray diffraction (Table. 1). By increasing the hot-rolling temperature, the ratio of the intensity of (0010) peak to that of (117) peak increased. As showed by Wu *et al* [1] the final heat treatment did not significantly improve the grain alignment, but is important for the enhancement of J_c due to the reduction of the cracks during the final rolling. Typically, the Ag/2212 interface is flat for cold-rolled samples but irregular for the hot-rolled samples. We attribute this to the different hardness of Bi-free phase and that of 2212 oxide as well as the softening of silver at the hot-rolling temperature.

Table 1 also shows magnetically measured T_c . All values were in the range of 80K-85K, with the tape rolled at 300 °C after pre-heating at 350 °C showing the highest value (~85K).

Fig. 3 SEM photomicrographs of thin longitudinal cross section of 2212 core after rolling: (a) first cold rolled, then partially melted; (b) first cold rolled then hot rolled at 400 °C (furnace: 750 °C), followed by partially melted; (c) same as (a), then cold rolled; (d) same as (c), followed by 840 °C for 100hrs; (e) same as (a), then hot rolled at 420 °C (furnace: 750 °C); (f), same as (c), followed by 840 °C for 100hrs.

Fig. 4 SEM photomicrographs of thin longitudinal cross section of Pt 2212 core by rolling: (a) first cold rolled, then partially melted; (b) same as (a), then cold rolled; (c) same as (b), followed by 840 °C for 100hrs; (d) same as (a), then hot rolled at 700 °C (furnace: 750 °C); (e) same as (d), followed by 840 °C for 100hr.

Fig. 5 (a, b, c) shows the magnetization $J_{cm}(H)$ for fields up to 5.5T ($H \perp c$) at 5K and 20K and the zero field transport J_{ct} (4.2K) for all samples. The magnetization $J_{cm}(H)$ was calculated using Bean's model, $J_c = 30\Delta M/d$, where d is the average diameter of the circulating loop. For rectangularly cross-sectioned tapes, the width of the oxide as measured by SEM was used. For both 2212 and Pt-2212 samples, $J_{cm}(H)$ increased with the hot-rolling temperature. Note, however, that no enhancement was obtained when increasing the hot-rolling temperature from 300°C (furnace 350°C) to 370°C (furnace 750°C), yet large enhancement resulted when the temperature was further increased to 420°C (furnace 750°C). Also marked in the Fig.5 (a, c) are the zero field transport J_{ct} for the 2212 and Pt-2212 samples. Transport J_{ct} for sample A4 is $1.25 \times 10^4 \text{ Acm}^{-2}$, and for the sample B3 is $3.46 \times 10^4 \text{ Acm}^{-2}$. The dopant Pt slightly enhanced the transport J_{ct} . We attributed the increased J_{ct} by hot-rolling to the improved grain alignment in the core and to the core densification.

Fig. 5. Critical current densities $J_{cm}(H)$ at 5K, 20K and J_{ct} at 4.2K, zero field for 2212 and Pt-2212 tapes: (a) 2212 at 5K; (b) 2212 at 20K; (c) Pt-2212 at 5K and 20K.

In hot-rolling, the Ag-clad tape is heated in a furnace and then quickly rolled. Through proper process design, this transfer time can be held to less than one second. Little heat

will be lost and the following analysis assumes that the tape holds its initial temperature until it contacts the rolls. The initial temperature of the tape is T_i and the roll temperature is T_r , with $T_i > T_r$. The roll diameter is R , its rotational speed is ω and hence the velocity of the tape through the rolls is $R\omega = U_0$. The process is illustrated schematically in Fig. 6.

The thickness of the Ag and the superconductor core are approximately the same. The thermal diffusivity of Ag⁸, α_{Ag} , at $T_i = 825^\circ\text{C}$ is $1.30 \text{ cm}^2/\text{s}$, that of a Bi-Sr-Ca-Cu-O core⁹, α_{sc} , is $\approx 10^{-3} \text{ cm}^2/\text{s}$, with extrapolation from 20°C to higher temperature based on data for typical ceramics listed in reference⁸. Since $\alpha_{Ag} \gg \alpha_{sc}$, it is assumed that the Ag sheath quenches quickly to the temperature of the rolls. (It will be shown later that this assumption is valid.) One must then examine heat flow from the superconductor to the Ag. The centerline of the core is defined as $y = 0$. When the tape first contacts the rolls, time $t = 0$, the temperature of the core is T_i , and the temperature at $y = b$ (the Ag/superconductor interface) is the roll temperature T_r .

If one neglects axial conduction, the governing heat-transfer equation is

$$k \partial^2 T / \partial y^2 = \rho C_p U_0 \partial T / \partial x \quad (1)$$

where k is the thermal conductivity of the superconductor, ρ is its density, and C_p is its specific heat.

$$\text{Let } U_0 = dx/dt, \quad (2)$$

$$\text{then } k \partial^2 T / \partial y^2 = \rho C_p \partial T / \partial t,$$

$$\text{or } \partial^2 T / \partial y^2 = 1/\alpha \partial T / \partial t, \quad (3)$$

with $\alpha = k / \rho C_p$. Let $T' = T - T_i$. Then, with boundary conditions at $t = 0$, $T' = 0$; $y = \pm b$, $T' = T_r - T_i$, the solution to Eq. 3 becomes¹⁰:

$$T^* = (T - T_i) / (T_r - T_i) = 1 - 4/\pi, \quad (4)$$

where $t^* = \alpha t / b^2$ and $y^* = y / b$.

Solutions expressed in dimensionless parameters are shown in Fig. 7. For the apparatus used in this work, the roll diameter was 13.3 cm and its speed was 30 revolutions/min. For a 200 μm tape reduced 10% in rolling¹, the contact length L is $\approx 1.63 \text{ mm}$. Thus,

$$\Delta t = L / U_0 = 1.63 \text{ mm} / 0.21 \text{ m/s} = 7.76 \times 10^{-3} \text{ s.}$$

$$t^* = \alpha \Delta t / b^2, \text{ with } b \approx 5 \times 10^{-3} \text{ cm. Thus,}$$

$$t^* = (10^{-3}) \times (7.7 \times 10^{-3}) / (5 \times 10^{-3})^2 = 0.3.$$

Fig.6. Schematic diagram of the tape during hot-rolling.

Fig. 7. Solutions for equ.(3), expressed in dimensionless parameters.

From Fig. 7, it can be seen that the superconductor core will cool significantly during rolling. It is noted that for a Ag layer of similar thickness, α is much larger and thus $t^* > 1$, which implies that the layer will quench to the temperature of the rolls. For the superconductor core, if, for example, $T_r = 400^\circ\text{C}$, then the temperature at the centerline of the core can be estimated

$$T^* \approx 0.4 = (T_{y=0} - T_i) / (T_r - T_i) = (T_{y=0} - 825^\circ\text{C}) / (400 - 825^\circ\text{C})$$

$$T_{y=0} \approx 655^\circ\text{C}$$

This analysis is approximate. The value of α_{sc} is based on extrapolation and axial conduction has been ignored. It is clear that the Ag sheath will quickly reach the roll temperature. This may, in fact, be an advantage. It may also be advantageous to increase the temperatures of the rolls above 400°C . However, the mechanical properties of the Bi-Sr-Ca-Cu-O superconductors are not well known at high or intermediate temperatures, although temperatures close to 700°C may be sufficient to induce significant plasticity^{11,12}.

CONCLUSION

Large current densities $J_{cm}(H)$ up to $1.6 \times 10^5 \text{ Acm}^{-2}$ at 5K, ~2T were obtained from the 2212 tape. The optimal hot-rolling for such sample was accomplished by pre-heating the rolls to 420°C with infrared heaters and rolling the tape directly from the furnace at 750°C , followed by an 840°C for 100hr final heat treatment. Samples were pre-heated in the furnace for about 10 minutes before hot-rolling. Better grain alignment was obtained with increasing of the hot-rolling temperature. The increased current density is attributed to the improvement of grain alignment during the hot-rolling. The Bi-free phases were crushed by rolling and reduced in size after the final heat treatment. Such effects are also beneficial to large current density. However, as the Ag/2212 interface became rough during hot-rolling, further improvements are expected by using a stiffer sheath material.

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