Fabrication of $Bi_2Sr_2CaCu_2O_x$/Ag superconducting tape using a screen-printing method

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High-T_c superconducting $Bi_2Sr_2CaCu_2O_x$/Ag tape was successfully fabricated using a screen-printing method and a partial-melting process. A highly oriented layer structure was achieved and confirmed by X-ray diffraction (XRD), pole-figure measurement and scanning electron microscopy (SEM). The critical current density, J_c, of the tape at 77 K, 0 T, was about 20 000 $A cm^{-2}$. High-temperature XRD was used to clarify the mechanism of the grain alignment. An aligned structure of the 2212 phase was originated from Bi-free compounds, such as $(Sr,Ca)CuO_2$ and $(Sr,Ca)_2CuO_3$ developed during a holding stage at 875 °C.

1. Introduction

Increasing the critical current density has been the major issue in the practical application of superconducting materials. A highly aligned microstructure is essential for a high J_c-value because a low J_c-value usually results from the grain-boundary weak-coupling problem as well as a random growth habit of the superconducting grains.

A highly textured 2212 superconductor has been successfully prepared by doctor-blade and partial-melt growth methods [1-3]. Silver-sheathed techniques have also been used by many researchers [4-7], but it seems difficult to control the various processing conditions such as drawing, swagging and rolling. In the former method the free surface of the superconducting materials which is exposed to air or oxygen during heat treatment, plays an important roll for the textured microstructure.

The grain alignment of the 2212 phase caused by partial-melt processing and a slow-cooling heat treatment in the doctor-blade method is strongly influenced by the thickness of the superconducting oxide layer. It has been reported that a highly aligned structure was observed for a tape whose final oxide layer was thinner than 20 μm [8]. From the viewpoint of easy control of the thickness of the oxide layer, the screen-printing method can be usefully adopted for the fabrication of superconducting tape.

In this study, 2212/Ag superconducting tapes were fabricated by a combination of screen-printing, partial melting, and slow-cooling processes. The implication of the results is discussed from the viewpoint of microstructural improvement and phase analysis.

2. Experimental procedure

Fig. 1 shows a flow chart of the overall process. Starting powders of Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO were mixed with a nominal composition of Bi:Sr:Ca:Cu: $= 2:2:1:2$. The powder mixtures were ball milled and calcined twice at 800 ° C and 820 °C for 12 h, respectively. Synthesized 2212 powder was mixed with an organic vehicle (such as a solvent, binder and plasticizer) by means of a planetary ball mill. This paste was printed onto a silver tape about 15 μm thick through a 300-mesh silk screen. After removal of the binder at 600 °C for 24 h, a differential thermal analysis (DTA) measurement was performed to establish the partial-melting temperature of the 2212/Ag tape. The printed 2212/Ag tape was heat treated in the way shown in Fig. 2. The alignment of 2212 grains was
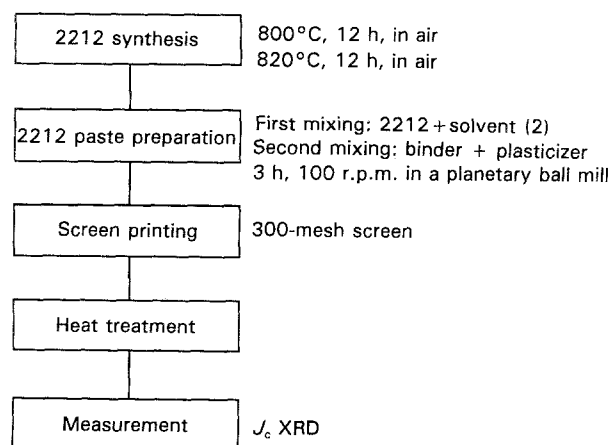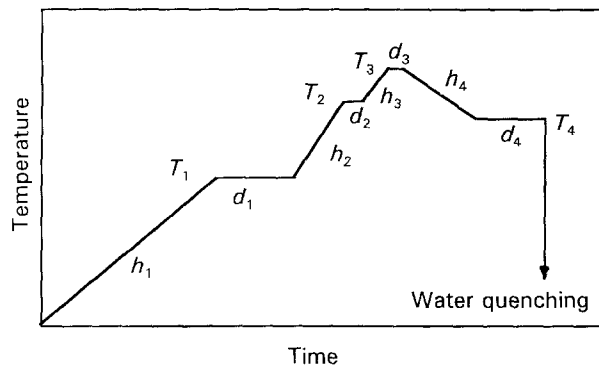
2212 synthesis	800°C, 12 h, in air / 820°C, 12 h, in air
2212 paste preparation	First mixing: 2212 + solvent (2) / Second mixing: binder + plasticizer / 3 h, 100 r.p.m. in a planetary ball mill
Screen printing	300-mesh screen
Heat treatment	
Measurement	J_c XRD

Figure 1 Schematic flow chart of the experiment.

Figure 2 Heat-treatment schedule.

Temperature (°C)	Heating rate, °C min^{-1}	Holding time, d
T_1 600	h_1 0.5	d_1 24 h
T_2 830	h_2 5	d_2 15 min
T_3 865–890	h_3 10	d_3 5–30 min
T_4 825	h_4 5	d_4 1 h

Figure 3 DTA curve for the screen-printed 2212/Ag tape.

examined by X-ray diffraction (XRD) (Rigaku, D-max 3C), in which the pole-figure measurement was made using the Shultz reflection method. The changes in phases during the heating, holding and cooling processes were examined using high-temperature XRD (Rigaku, D-max 3C). Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) was used to analyse the microstructure and the phases. The measurement of J_c was by the standard four-probe method at 77 K in a zero magnetic field.

3. Results and discussion

The 2212 single phase was obtained after calcinating twice; it was confirmed by XRD. It is well known that the most effective method of increasing the J_c-value in
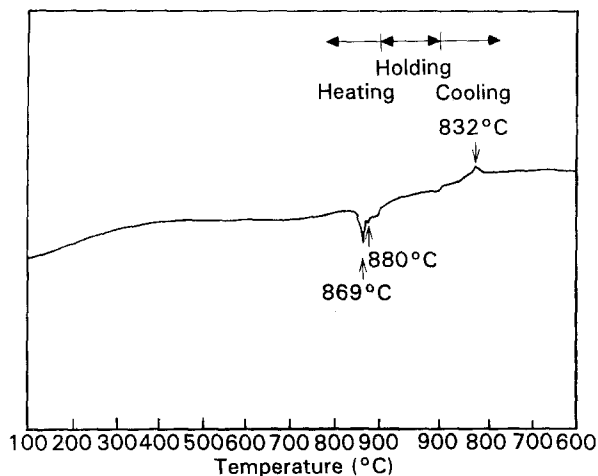
2212/Ag tape is the introduction of a partial-melting process during heat treatment followed by slow cooling. But, the partial-melting temperature of 2212/Ag tape depends on the processing parameters such as the thickness of the oxide layer and the kind of substrate. Thus, DTA measurement was necessary to find out the partial-melting temperature of 2212/Ag tape.

Fig. 3. shows a DTA result for 2212/Ag tape measured during heating to 900 °C at a rate of 5 °C min^{-1}, holding for 30 min and cooling at a rate of 5 °C min^{-1}. An endothermic peak appeared at 869 °C during heating which corresponds to the partial-melting temperature of 2212/Ag tape. It has been reported that a melting temperature of the 2212 phase of 870 °C was observed by an *in-situ* X-ray investigation [10]. The onset temperature of this endothermic peak is 854 °C, that is, relatively lower than the melting temperature of the 2212 phase. The appearance of melts at
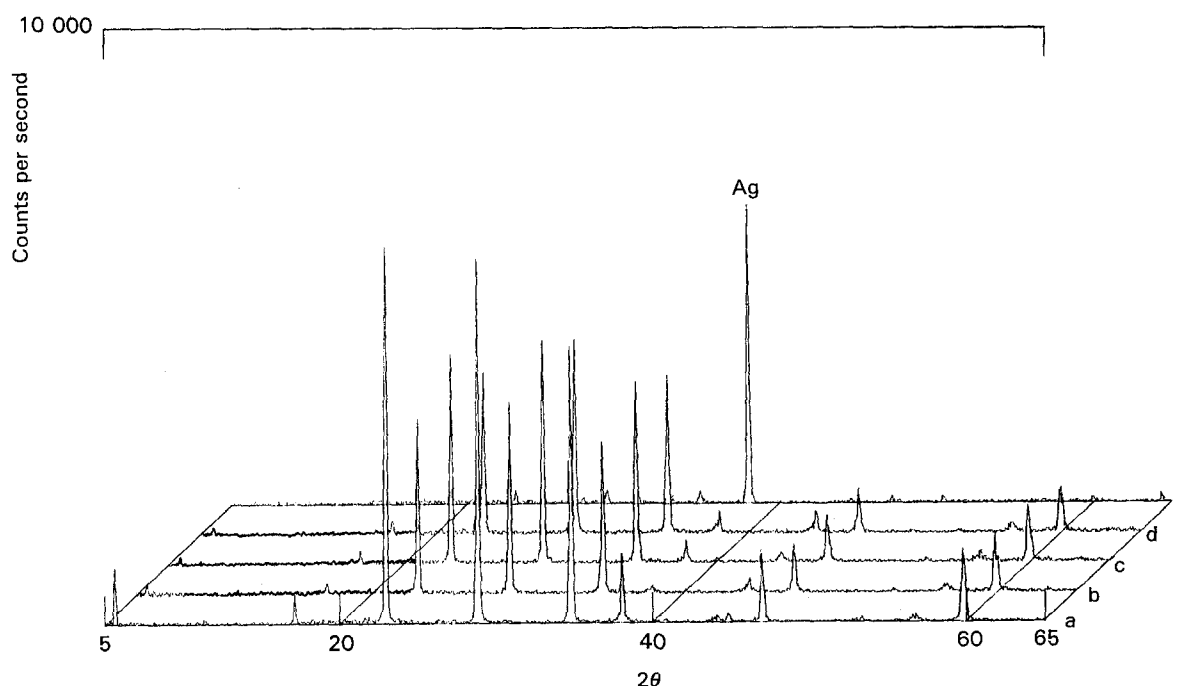

Figure 4 XRD patterns for the specimens heat treated for 5 min at various temperatures (T_3) : (a) 885 °C, (b) 880 °C, (c) 875 °C (d) 870 ° and (e) 865 °C.

lower temperatures might result from eutectic melting between the oxide and silver [9]. The small endothermic peak at 880 °C during heating might be related to the decomposition of a Bi-free compound such as $(Sr,Ca)_1Cu_1O_2$ which was produced by the decomposition of 2212 phase. The exothermic peak at 832 °C during cooling corresponds to the recrystallization of the 2212 phase from the Bi-rich liquid phase and a Bi-free compound such as $(Sr,Ca)_1Cu_1O_2$ and $(Sr,Ca)_2Cu_1O_3$. The formation of these phases will be discussed later in detail.

Fig. 4. shows the XRD patterns of the screen-printed 2212/Ag tape heat treated below and above the partial-melting temperatures of the 2212 phase for 5 min followed by slow cooling and quenching as shown in Fig. 2. The specimen heat treated at 865 °C for 5 min, just below its partial melting temperature, did not show remarkable development of the (0 0 1) plane of the 2212 phase. The slight development of the (0 0 1) plane at 865 °C was mainly due to the inherent effect of the screen-printing method. The specimen heat treated at temperatures higher than the partial-melting temperature showed remarkable development of the (0 0 1) plane. This suggests strongly that the development of the (0 0 1) plane is sensitive to the formation of a liquid phase, that is, the presence of sufficient liquid phase seems to be essential for grain alignment.

The J_c-values of these specimens are plotted as a function of temperatures (T_3) in Fig. 5. In spite of the high degree of c-axis alignment, the J_c values were generally low. The texturing of the 2212 phase is not intensive because the alignment of the 2212 phase has produced only near the surface of the specimen at the low T_3 temperature. The undesirable compositional change due to the evaporation of superconducting phases at high T_3 temperatures seems to be responsible for these low J_c-values. It has been reported that
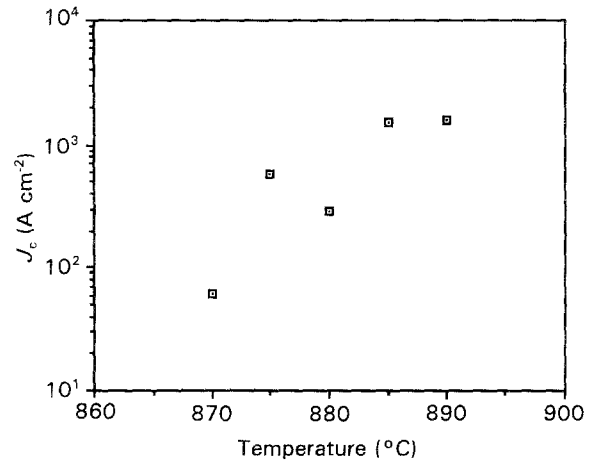

Figure 5 J_c of the specimens heat treated at various temperatures (T_3) for 5 min.

2% of the total Bi was lost below 900 °C [10]. Thus, the optimum conditions for the temperature (T_3) and the holding time (d_3) have to be determined to obtain high J_c-values. In this study, the optimum temperature, T_3, was fixed at 875 °C to avoid an undesirable compositional change and the holding time, d_3, was varied from 5 to 30 min to establish the optimum holding time.

Fig. 6. shows XRD patterns of the specimens heat treated at 875 °C for 5, 15 and 30 min. The peak intensity of the (0 0 1 0) plane of the 2212 phase is plotted with the holding time (d_3) in Fig. 7. The intensity of the (0 0 1 0) plane for the sample heat treated for 15 min was the highest. The J_c-values of these specimens are shown in Fig. 8 and the sample heat treated for 15 min also had the highest J_c-value $(20000\,A\,cm^{-2}, 77\,K, 0\,T)$. Therefore, it should be noted that the heat treatment at 875 °C for 15 min is the optimum processing condition in this study. Fig. 9
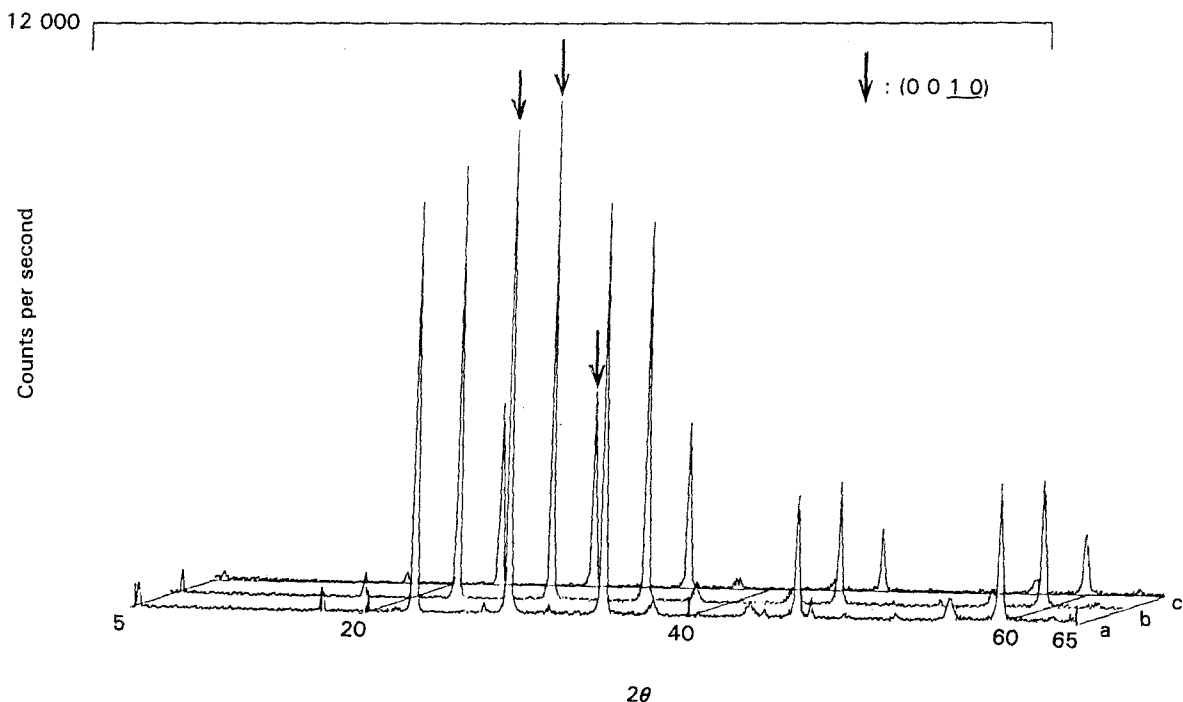

Figure 6 XRD patterns for specimens heat treated at 875 °C for: (a) 5 min, (b) 15 min, (c) 30 min.
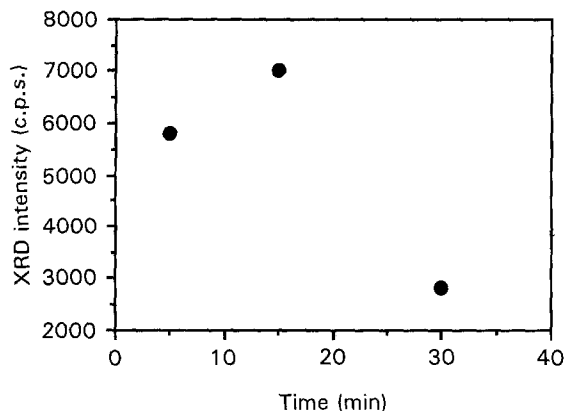
Figure 7 The peak intensity (in counts per seconds, c.p.s.) of the (0 0 1 0) plane of the 2212 phase plotted against the holding time (d_3) at 875 °C.
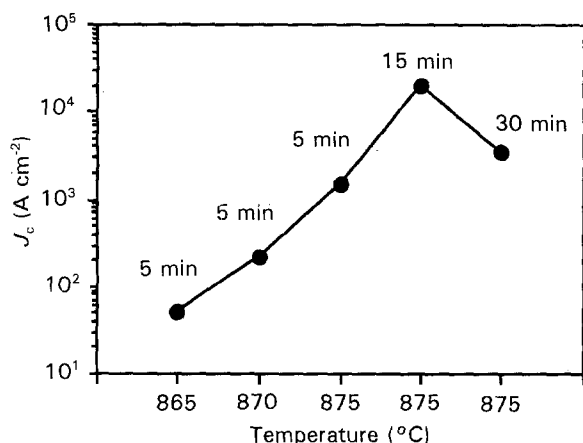

Figure 8 The value of J_c of specimens heat treated at various temperatures (T_3) and holding times (d_3). (77 K, 0 T.)
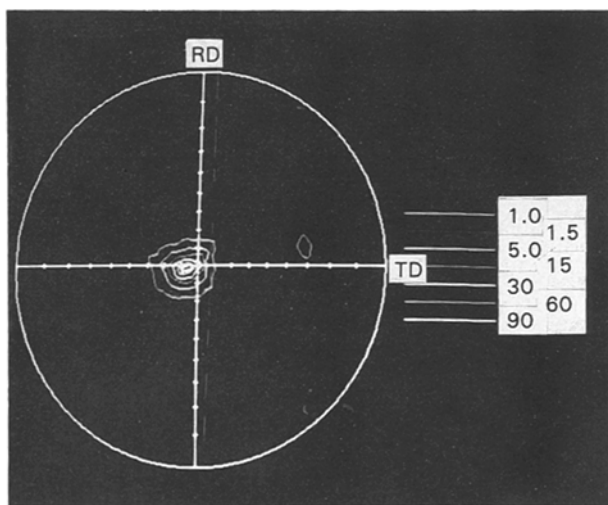

Figure 9 The pole figure using the (0 0 1 0) diffraction lines of the 2212/Ag tape heat treated at 875 °C for 15 min then slow cooled and quenched.

shows the pole figure obtained by using (0 0 1 0) diffraction lines for the sample heat treated at 875 °C for 15 min. The pole figure reveals the maximum intensity at the centre and intensity contours around the centre, suggesting that the (a–b) plane of the 2212 phase is aligned well parallel to the silver-tape surface.

Fig. 10 shows a SEM micrograph of the fractured cross-section of the specimen heat treated at 875 °C for 15 min. A highly aligned microstructure can be clearly observed in Fig. 10. To find out whether this alignment occurred during the slow cooling or the holding at 875 °C, a SEM micrograph of the fractured surface of the sample quenched in ice water (from 875 °C) was also taken (Fig. 11). The quenched sample also shows an aligned structure, suggesting that grain alignment largely occurred during the holding period at 875 °C.

Fig. 12 shows a SEM micrograph and EDS analyses of the surface of the specimen heat treated at 875 °C for 30 min then quenched in ice water. The SEM micrograph consists mainly of plate-shaped grains and a glassy matrix. The EDS analyses suggest that the plate-shaped grains are Bi-free compounds such as (Sr,Ca) CuO_2 (Fig. 12b) and $(Sr,Ca)_2CuO_3$ (Fig. 12c), and a matrix (Fig. 12d) composed of a Bi-rich liquid phase including a 2201 phase. The presence of a 2201 phase in this specimen was confirmed by an XRD study. But this specimen does not contain the 2201 phase at a high-temperature stage, as will be shown in the results of a high-temperature XRD study later. This suggests that the 2201 phase may have been
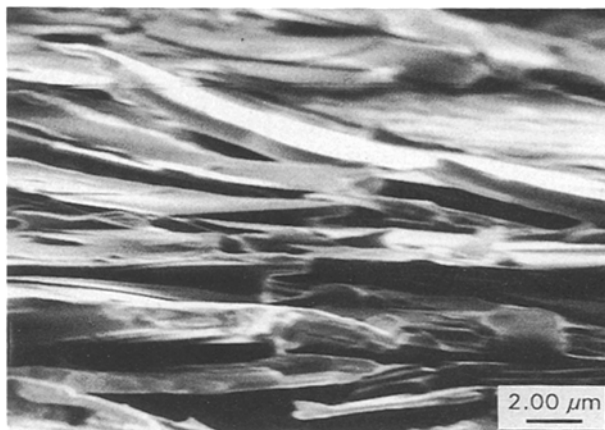

Figure 10 A SEM micrograph of the fractured cross-section of the specimen heat treated at 875 °C for 15 min then slow cooled and quenched.
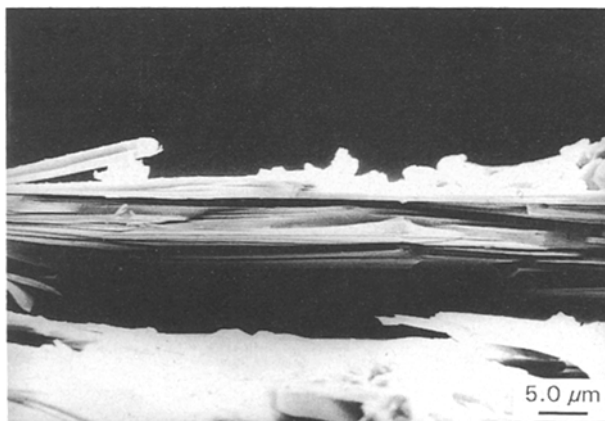

Figure 11 A SEM micrograph of the fractured cross-section of the specimen heat treated at 875 °C for 15 min then quenched.
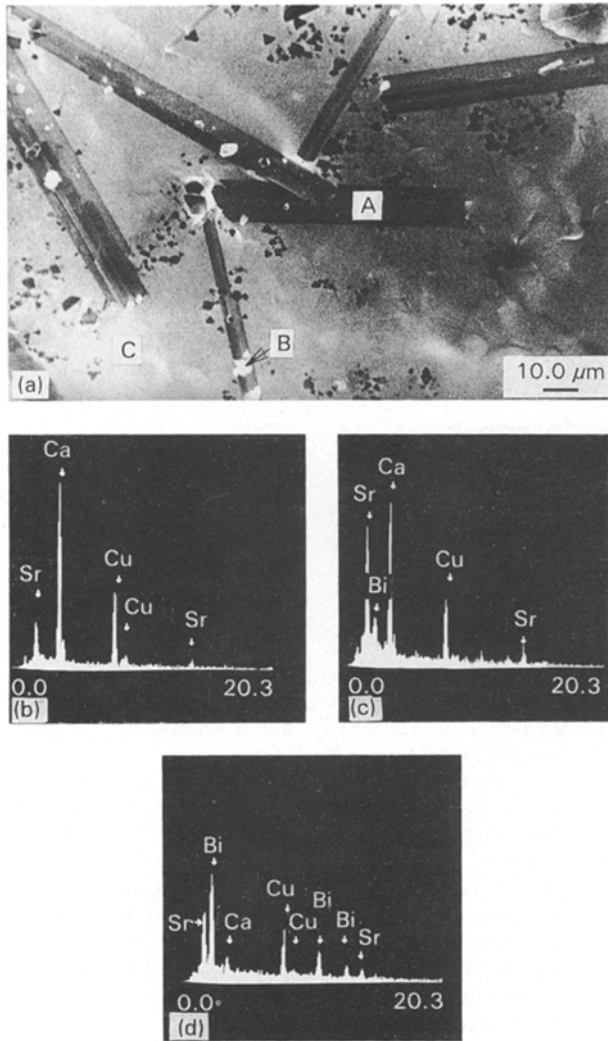
directly crystallized from the melts (that is, the Bi-rich liquid phase) during quenching. The presence of these phases was also confirmed by high-temperature XRD.

The changes in the crystalline phases during the heating, holding and cooling processes were investigated directly by using high-temperature XRD (Fig. 13). High-temperature XRD of 2212/Ag tape was performed during heating to 875 °C at a rate of 1 °C min^{-1}, holding for 33 min and cooling at a rate of 1 °C min^{-1}. It was noted that only the 2212 phase was detected during the heating process. From 869 °C, the peak intensity of the 2212 phase diminished fast and two new peaks at $2\theta = 44°$ and $54°$ grew during the holding process. It has been reported that the peak at $2\theta = 44°$ corresponds to orthorhombic $(Sr,Ca) CuO_2$ and the peak at $2\theta = 54°$ corresponds to orthorhombic $(Sr,Ca) CuO_2$ and the peak at $2\theta = 54°$ corresponds to orthorhombic $(Sr,Ca)_2CuO_3$ [10]. It is direct evidence of the alignment of Bi-free compounds in the molten state that the peaks at $2\theta = 54°$ correspond to the low index, $(0\,0\,2)$, of $(Sr,Ca)_2CuO_3$. The intensity of these peaks increased up to 15 min and then diminished at longer holding times. It can be supposed that Bi-free compounds were produced by the decomposition of the 2212 phase at 875 °C up to 15 min and then gradually dissolved into the Bi-rich liquid phase, indicating that this processing condition provides the highest frequency of Bi-free compounds in the melts. This may be responsible for the highest value of J_c in the specimen heat treated at 875 °C for 15 min. When Bi-free compounds were developed in sufficient amounts of the Bi-rich liquid phase, these compounds floated on the surface due to their density being lower than the Bi-rich liquid phase as shown in Fig. 12. This effect acts as a driving force for grain alignment
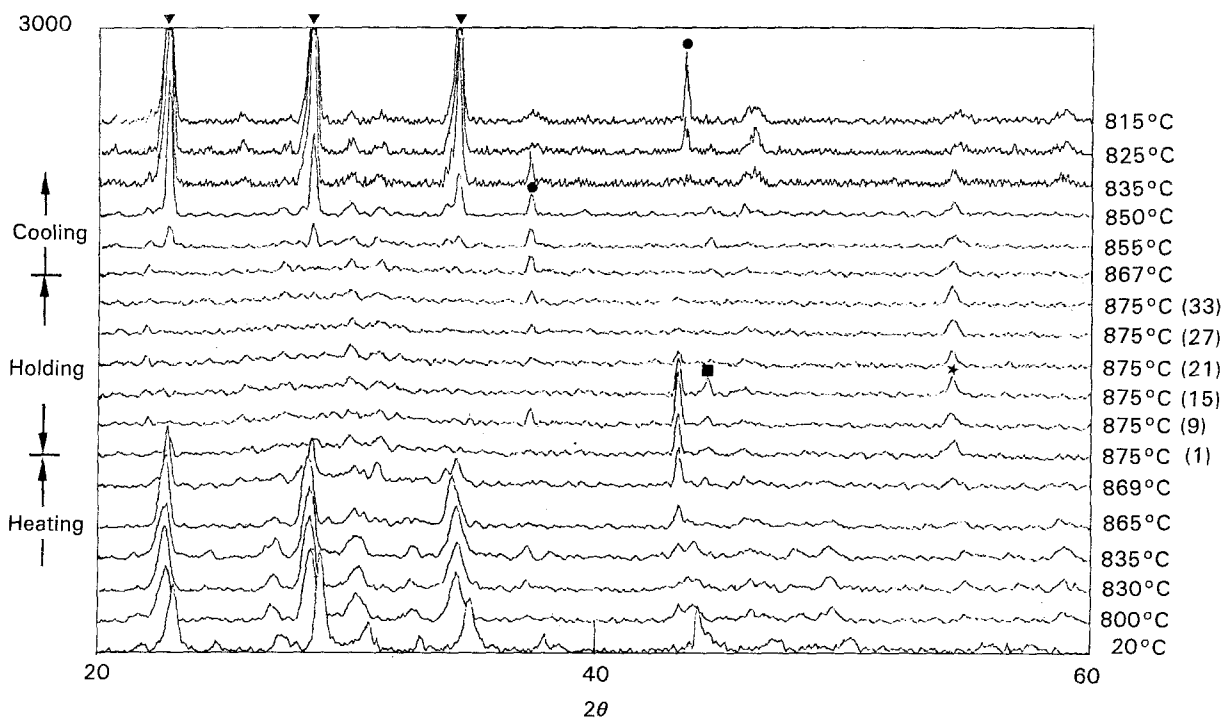
Figure 12 A SEM micrograph and EDS analyses of the surface of the specimen heat treated at 875 °C for 30 min then quenched.

Figure 13 High-temperature XRD patterns of 2212/Ag tape: ($\blacktriangledown$) 2212 phase ($\blacksquare$) $(Sr,Ca)_1Cu_1O_2$, (*) $(Sr,Ca)_2Cu_1O_3$, and ($\bullet$) Ag.

because the Bi-free compounds $(Sr,Ca)CuO_2$ and $(Sr,Ca)_2CuO_3$, have orthorhombic structures and grow with their c-axis perpendicular to the surface. The effect of the free surface of melts on the texture of the 2212 phase has also been reported by other researchers [11]. They have observed, by a method of *in-situ* high-temperature microscopy, that the crystals floated in the solution at the first stage of the growth process. During the cooling process, the peak intensity of the Bi-free compounds diminished and peaks of the 2212 phase appeared again. This suggests that the 2212 phase formed from Bi-free compounds and the Bi-rich liquid phase. The slow cooling process during the heat treatment might be necessary to provide sufficient time for the formation of the 2212 phase from Bi-free compounds and the Bi-rich liquid phase. Even after a long period of processing, small amounts of Bi-free compounds remained in the specimen due to unstoichiometric compositions resulting from the volitilization of Bi.

4. Conclusion

A 2212/Ag superconducting tape was fabricated by a screen-printing method. A highly oriented layered structure was achieved by suitable heat treatment, which consisted of partial melting and a slow cooling process. The critical current density was very sensitive to the heat-treatment temperature and the holding time. The highest value of J_c was obtained when the 2212/Ag tape was heat treated at 875 °C for 15 min followed by slow cooling and quenching. Its value was $2 \times 10^4 \, A \, cm^{-2}$ at 77 K and 0 T.

A high temperature XRD study of 2212/Ag tape was used to clarify the grain alignment of the 2212 phase. It was found that the 2212 phase decomposed to Bi-free compounds such as $(Sr,Ca)CuO_2$ and $(Sr,Ca)_2CuO_3$ and a Bi-rich liquid phase near 870 °C. An aligned grain structure originated from these Bi-free compounds, developed as a layered structure during the holding process at 875 °C. Finally, a highly aligned 2212 phase was transformed from an aligned Bi-free phase during slow cooling.

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