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Texture formation in superconducting BSCCO 2212/Ag composite tapes
Effect of cold rolling and laser float zone melting technique

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Abstract

Bi-2212/Ag composite tapes were fabricated by the doctor blade casting method and then subjected to thermomechanical processing and a laser float zone melting technique, in order to compare the texture developed by these two techniques. The effect of the processing parameters, of the above two different methods, on the texture formation of 2212 phase was monitored by θ–2θ X-ray diffraction patterns, pole-figure studies, and by scanning electron microscopy. Although mechanical deformation yielded a moderate texture, the microstructure of the cold-rolled and solid-state sintered 2212/Ag tape shows the presence of pores and "weakly linked" grains. With a laser float zone melting technique, much better texture could be obtained, and it is shown that this texture improves as the scanning rate decreases.

1. Introduction

Of the three major families of high-temperature superconductors, $YBa_2Cu_3O_{7-x}$, Bi–Sr–Ca–Cu–O, and Tl–Ba–Ca–Cu–O, the Bi based superconductor may be the most promising candidate for high magnetic field applications due to its high critical magnetic field (H_{c2}) as well as a high superconducting transition temperature (T_c) [1,2]. In the Bi based superconductor, there exist three superconducting phases with three different numbers of Cu–O layers in a crystal unit cell: 10 K phase, $Bi_2Sr_2CuO_x$ with a single Cu–O layer; 80 K phase, $Bi_2Sr_2CaCu_2O_x$ with two Cu–O layers; and 110 K phase, $Bi_2Sr_2Ca_2Cu_3O_x$ with three Cu–O layers. Throughout this paper, 2201, 2212, and 2223 refer to these three above mentioned superconducting phases, respectively.

In spite of these superior intrinsic properties of the Bi based superconductor, there exist some technical barriers which have to be overcome for successful practical applications. The most serious problem arises from the fact that the transport critical current density is extremely low in the conventionally sintered bulk Bi superconductors, because of such factors as high porosity and weak coupling between the superconducting grains [3]. Furthermore, the intrinsic brittleness of these ceramic superconductors makes it very difficult to fabricate them in the form of tapes or wires which are required for most practical engineering applications. This problem, caused by the brittle nature of these ceramic superconductors, has been greatly improved by forming superconductor/metal composites [4]. Ag has been known to be the best cladding material since it does not degrade the superconducting properties. In addition, Ag has some desirable secondary effects such as the en-

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hancement of texture near the Ag/superconductor interface [5–7]. In order to overcome the weak-link problem at grain boundaries, which is assumed to be the main reason for the low critical current density in the conventionally sintered bulk Bi superconductors, a strong crystallographic alignment of grains parallel to the *a–b* conduction planes is essential [8]. In this regard, several processing techniques have been developed to produce a dense and highly oriented microstructure. Melt processing has been proven to be the most effective technique for the texture development of a Bi-2212/Ag composite tape [9–11]. On the other hand, it has been shown that thermomechanical processing is more suitable for Bi-2223/Ag tape because of the difficulty of 2223 phase growth from the melt [12,13].

While thermomechanical processing has been successfully used to develop a texture for the Bi-2223/Ag tape, there are not many references in the literature on the texture development by this technique for Bi-2212/Ag tape. Considering that these two phases have a similar structure, and that the Bi-2212/Ag tape is subjected to mechanical deformation for the purpose of densification before the final heat treatment in most of the melt processing, it is considered worthwhile to investigate the effect of mechanical deformation on the texture development of Bi-2212/Ag tape.

In this paper, first we report the effects of cold rolling and subsequent annealing on the texture formation of Bi-2212/Ag tape. Next, this deformation-induced texture is compared with the texture formed by a laser float zone melting technique, which was developed by us and applied to Bi-2212/Ag tape production.

2. Experimental procedure

2212/Ag composite tapes for cold rolling and laser treatment were prepared by a doctor blade casting method. Initially, Bi-2212 powder was produced by the calcination of an appropriate mixture of Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO powders. The calcination was done at 850°C for 24 h. Then this 2212 powder was mixed with an organic material, consisting of a solvent (isopropanol) and a dispersant (glycerol), to make a slurry. The resulting slurry was cast on Ag foil, under a doctor blade, to produce a 2212/Ag composite green tape. The thickness of the Ag foil was ~0.3 mm and the resulting green tape was approximately 12 mm in width and 0.6 mm in thickness. The composite green tape was heated at 400°C for 2 h to remove the organic material, and then the temperature was increased to 850°C, and held for 3 h to produce an interfacial bonding between the Ag and the 2212 phase.

The 2212/Ag tapes were cold rolled down to a final thickness of 0.07 mm. To retain the ductility of the Ag, annealing was done at 500°C for 1 h for every 30% reduction of thickness. Two different rolling schedules were used in this study: one with a high thickness reduction ratio per pass (32–50% per pass), and the other with a lower thickness reduction ratio per pass (28–35% per pass). In the case of the high reduction ratio per pass, a total of four passes were carried out to achieve a final thickness of 0.07 mm. For the low reduction ratio case, a total of six passes were performed to achieve the same end result. The rolled tapes were sintered in solid-state for 4–100 h in the temperature range of 850–860°C, in order to promote grain bonding and grain growth.

A laser float zone melting technique was also applied to 2212/Ag tapes, which was prepared by the above mentioned doctor blade casting and cold rolling. This is done in order to compare the texture, formed by the above thermomechanical processing, with a texture induced by the laser float zone melting technique. Details of the experimental set-up and procedures were reported elsewhere [14]. Briefly, a 2212/Ag tape, 10 mm wide, 50 mm long, and 0.3 mm thick, was suspended vertically inside a furnace and heated up to 750°C. Under that condition, the tape transported downward while a stationary laser beam was allowed to enter through a hole on the furnace wall. The unfocused laser beam, from a 3 kw CW CO_2 laser, was chopped into a rectangular shape of 15×2.5 mm^2 before entering into the furnace. The temperature of the melted zone was measured by an optical pyrometer and controlled in the range of 890–950°C by varying the laser input power. The laser scanning rates (actually the motion of the sample) and power densities ranged from 10 mm/h to 13 mm/h, and from 40 W/cm^2 to 50 W/cm^2, respectively.

After rolling and laser scanning, X-ray diffraction patterns, and experimental pole figures were obtained from the surface of the tapes for phase identification and texture analysis. The 2212 grain size, grain morphology, grain alignment, and the presence of a secondary phase were examined on the polished cross section in the thickness direction of the tape by using a Hitachi S-2500C scanning electron microscope equipped with a Link energy dispersive X-ray analyzer.

3. Result and discussion

θ–2θ X-ray diffraction patterns and pole figure for the (0010) pole distribution of Bi-2212 phase have been widely used to observe the "c-axis alignment"

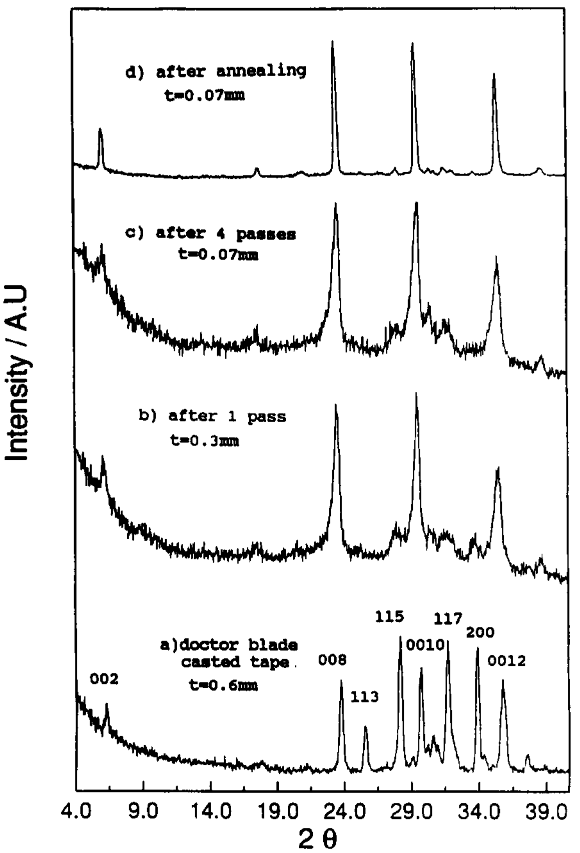

Fig. 1. X-ray diffraction patterns of successively cold-rolled and annealed 2212/Ag tape with a high reduction ratio per pass, (32–50% per pass): (a) doctor blade cast tape, (b) after 1 pass; thickness of 0.3 mm, (c) after 4 passes; thickness of 0.07 mm, (d) after annealing at 850°C for 24 h.

((00l) normal to the sample surface) of Bi-2212 phase. The pole figures, combined with θ–2θ X-ray diffraction patterns, offer a good overview of the c-axis alignment averaged over the length and width of a few mms. Fig. 1 shows the measured X-ray diffraction patterns of a successively cold rolled and annealed 2212/Ag tape with a high reduction ratio per pass (32–50% per pass). It can be seen that the doctor blade cast tape, Fig. 1(a), shows a random distribution of c-axis of 2212 grains, with the strongest diffraction peaks from the (115) and (117) planes. Thus, no preferential c-axis alignment of 2212 grains exists. Other than the major 2212 phase, a small amount of a second phase was also observed in the doctor blade cast tape, as indicated by a peak near the 2θ of around 30°. However, after a single pass of rolling (Fig. 1(b)), the intensities of these non-(00l) peaks were greatly reduced while the intensities of the (008), (0010) and (0012) peaks were sharply increased. This result indicates the formation of a strong texture with the c-axis of 2212 grains perpendicular to the tape surface.

The formation of this c-axis alignment is thought to be mainly due to the compressive force imparted to the sample during the rolling. In the Bi superconductors, grain growth is much faster along the crystallographic a and b directions than along the c-direction, so the growing grains assume a plate-like morphology with a high aspect ratio [15]. The compressive force during rolling causes these plate-like 2212 grains, with random distribution of their c-axis with respect to tape surface, to fracture and rotate. The rotation of the grains is prohibited once the grains are oriented with their c-axis perpendicular to the tape surface, which is the stable position for this morphology. The high porosity in doctor blade cast tape appears to have aided texturing, because the available free space allows an easier rotation of the grains during the first pass of rolling. With further rolling (Fig. 1(c)), the improvement in texture was not very significant. Only a small reduction of the (200) peak intensity was observed and the intensity of the (115) and (117) peaks remained at the previous intensity levels. This is because there is not much freedom to rotate the grains into a preferred orientation once the grains contact each other closely after the initial pass(es) of rolling.

A slight improvement in texture was also observed

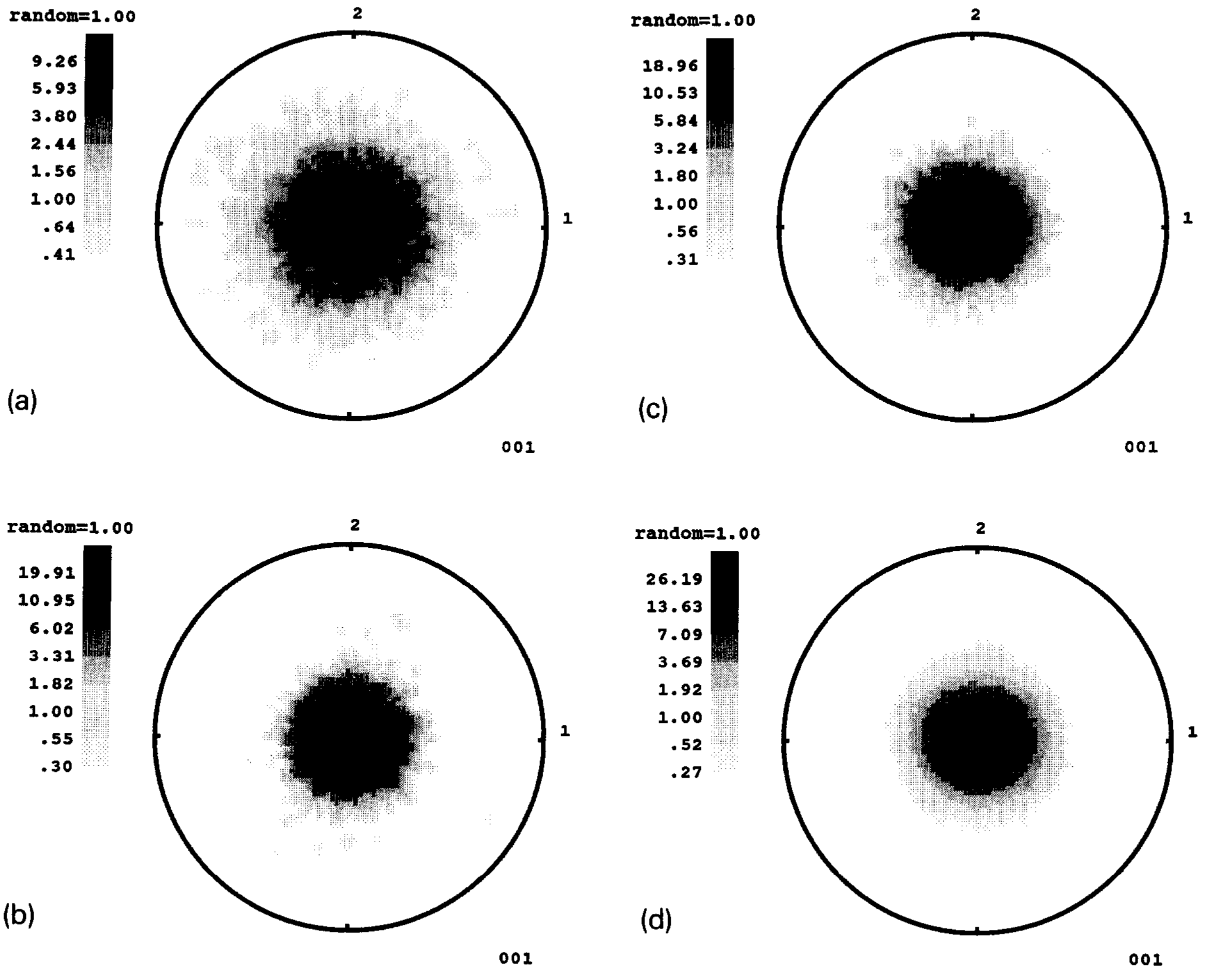

Fig. 2. Experimental $(00\underline{10})$ pole figures for successively cold-rolled and annealed tape: (a) doctor blade cast tape, (b) after 1 pass; thickness of 0.3 mm, (c) after 4 passes; thickness of 0.07 mm, (d) after annealing at 850°C for 24 h.

with the annealing of rolled tape as can be seen in a further decrease of the intensities of the (115) and (117) peaks (Fig. 1(d)). This is thought to be due to the preferential growth of the already aligned grains, formed during the cold-rolling stage, at the expense of the neighboring smaller misoriented grains [15]. In contrast, misoriented grains are much more difficult to grow since their growth is hindered by the abundance of aligned grains.

Although θ–2θ X-ray diffraction patterns provide an overview of overall texture, more useful information about texture, such as the accurate degree of alignment between the crystal orientations and the substrate normal, can be obtained from X-ray pole-figure analysis. Fig. 2 shows experimental $(00\underline{10})$ pole figures from the top surface of a successively rolled and annealed 2212/Ag tape. The $(00\underline{10})$ pole figure for the as-cast tape (Fig. 2(a)) shows a weak c-axis alignment. The width of the angular distribution of $(00\underline{10})$ poles is quite broad and the intensity of the center is relatively low. However, after one pass of rolling, clustering of $(00\underline{10})$ poles around the center and a sharp increase in the intensity of the center can be seen (Fig. 2(b)). This indicates that the random grains become progressively oriented in such a way that the $[00\underline{l}]$ directions become perpendicular to the tape surface and this observation is consistent with the θ–2θ X-ray diffraction results. The formation of

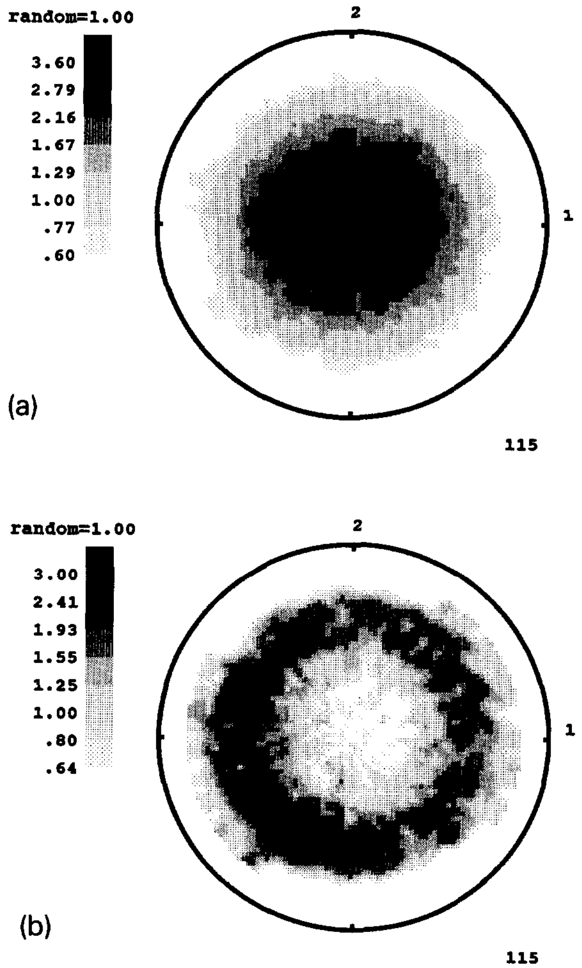

Fig. 3. Experimental (115) pole figures for cold-rolled tape: (a) doctor blade cast tape and (b) after first pass of rolling; thickness of 0.3 mm.

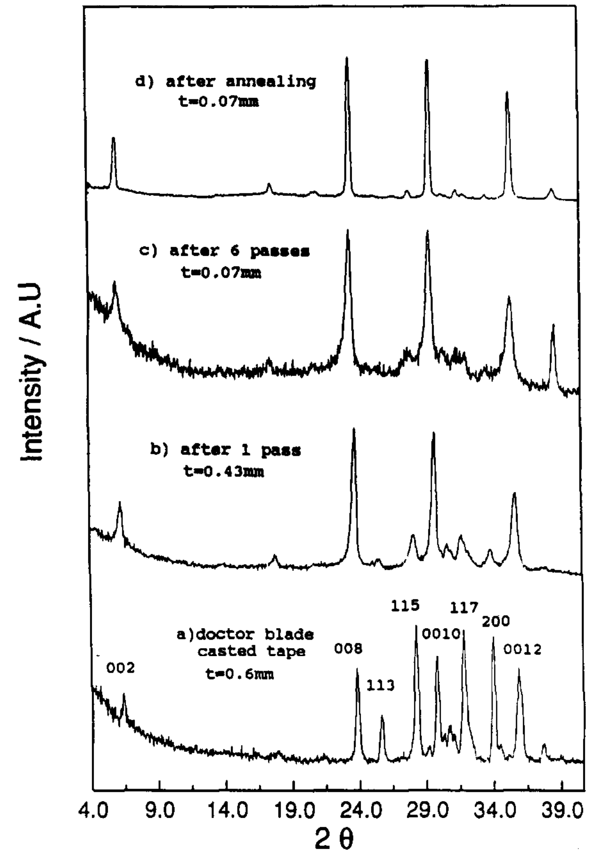

Fig. 4. X-ray diffraction patterns of successively cold-rolled and annealed 2212/Ag tape with a low reduction ratio per pass, (28–35% per pass): (a) doctor blade cast tape, (b) after 1 pass; thickness of 0.43 mm, (c) after 6 passes; thickness of 0.07 mm, (d) after annealing at 850°C for 24 h.

this *c*-axis alignment that occurred during the first pass of rolling can be more clearly seen in (115) pole figures of the same tape (Fig. 3). Fig. 3(a) indicates that the (115) planes are nearly parallel to the doctor blade cast tape, rather than the desired (00*l*) planes. With a first pass of rolling (Fig. 3(b)), (115) poles move toward the outside of the figure and form a circular band, while (00*l*) poles rotate in such a way as to produce a clustering at the center of the (0010) pole figure as shown in fig. 2(b). Further rolling does not show much improvement of the *c*-axis alignment as can be seen in Fig. 2(c). Annealing, followed by rolling, slightly improved the texture as can be concluded by the slight decrease of the width of the angular distribution of the poles, and an increase of the intensity (Fig. 2(d)).

In order to investigate the effect of the rolling parameters on the texture formation, and to find an optimum rolling condition for texture development, rolling with a different set of parameters was also carried out. Fig. 4 shows X-ray diffraction patterns for successively cold rolled and annealed 2212/Ag tape, with a low reduction ratio per pass (28–35% per pass). Again, most of the alignment occurred during the first pass of the rolling, although there still remains a considerable amount of (115), (117), and (200) peaks as compared with the X-ray diffraction

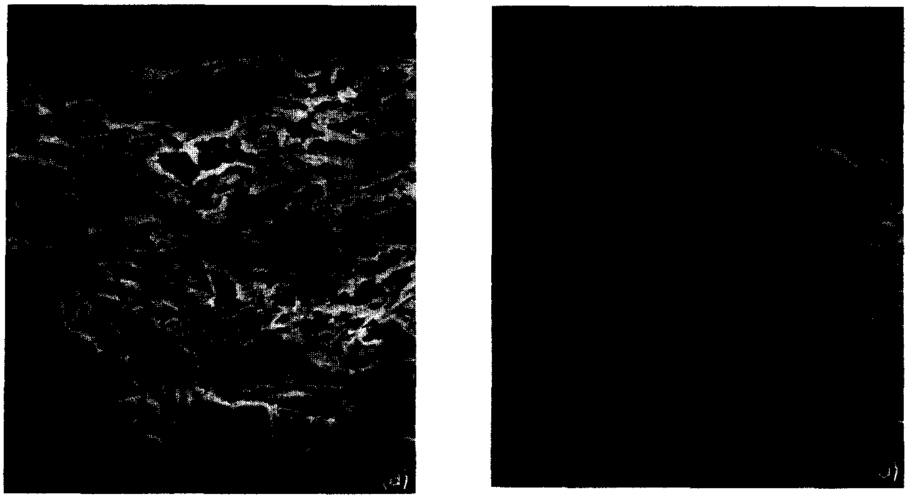

Fig. 5. SEM photographs of polished and etched longitudinal cross-section of 2212/Ag tape which was rolled down to 0.07 mm at a high reduction ratio per pass, and then annealed at 850°C for (a) 24 h and (b) 100 h.

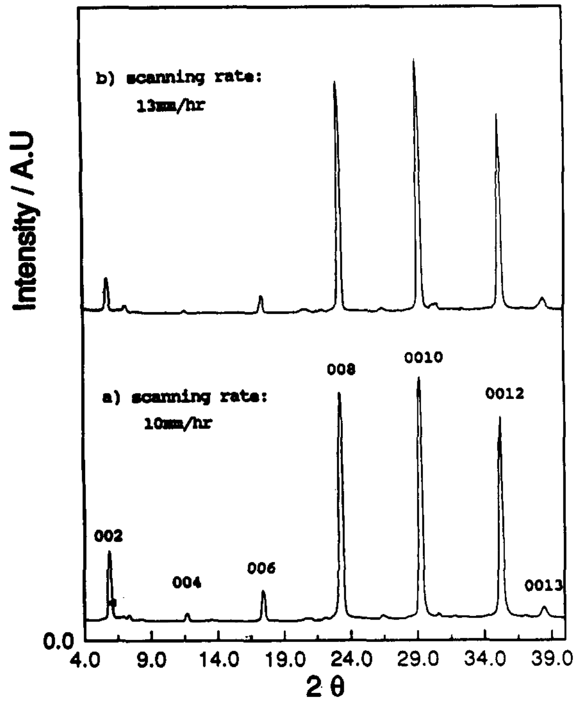

Fig. 6. X-ray diffraction patterns from the top surface of the laser-treated tape with a melted zone width of 2.5 mm: (a) scanning rate of 10 mm/h and (b) scanning rate of 13 mm/h.

pattern of the tape which was rolled at a high reduction ratio per pass. However, with further rolling and annealing, it eventually attained about the same degree of texture as that for the high reduction ratio per pass.

To confirm the textured microstructure, we performed SEM studies on the longitudinal cross-section of the rolled and annealed 2212/Ag tapes. Fig. 5 shows the polished and etched longitudinal cross-section of 2212/Ag tape, which was rolled down to 0.07 mm and annealed at 850°C for 24 h and 100 h (Figs. 5(a) and (b), respectively). Fig. 5 clearly shows that most of the plate-like grains are moderately aligned along the rolling direction, parallel to the tape surface. However, the grain size is very small, less than 10 μm, in the short-time annealed tape, and even long-time annealing causes only a limited grain growth. Moreover, in some regions of both samples, small pores were observed and grain coupling was seen to be poor, which would lead to inferior current carrying capacity.

While thermomechanical processing of 2212/Ag composite tapes did not yield a satisfactory alignment, a better texture was obtained by applying a laser float zone melting technique. We already reported some advantages of this technique, and the resulting improved c-axis alignment of 2212/Ag tapes [14]. Fig. 6 shows X-ray diffraction patterns from the top surface of the laser treated tapes. The top and bottom patterns, in this figure, correspond to a scanning rate of 13 mm/h and 10 mm/h, respectively. In both cases, the temperature of the melted zone was kept between

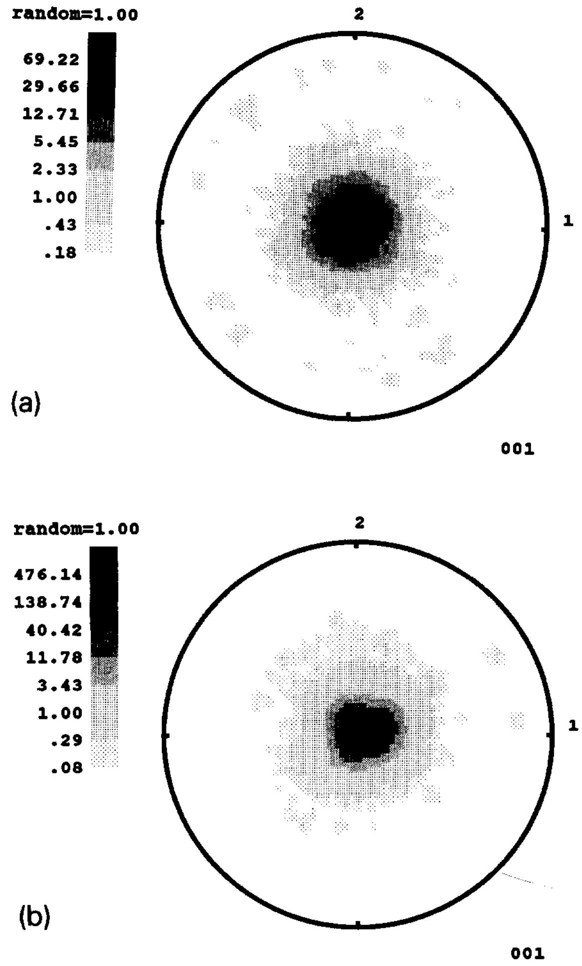

Fig. 7. Experimental $(00\underline{10})$ pole figures for laser-treated tape surface with a melted zone width of 2.5 mm: (a) scanning rate of 13 mm/h and (b) scanning rate of 10 mm/h.

940–950°C. These processing parameters give a temperature gradient of about 260°C/cm, which is about three times steeper than that of the tapes scanned with a melted zone width of 5 mm, which was used in our previous study. At this temperature, 2212 grains appear to melt completely and the deformation-induced texture by cold rolling is totally lost. Instead, new grains grow from the melt and align by a different mechanism. X-ray results for the fully processed tapes indicate that tapes, produced by both of the above mentioned scanning rates, are highly textured. The weak peaks from (115) and (117), which were still present in the cold-rolled and annealed tapes, are almost undetectable. This improved *c*-axis alignment was confirmed by the $(00\underline{10})$ pole figures for these tapes, as shown in Fig. 7. The clustering of $(00\underline{10})$ poles around the center of the projection becomes much stronger than that of the tapes which was heavily deformed and annealed (Fig. 2(d)). Further, the slowly scanned sample yielded a better texture than the fast scanned sample, which can be seen to produce a further decrease of the width of angular distribution of poles. Fig. 8 shows the SEM photographs of these samples. Both samples show a very dense microstructure with a 2212 layer of about 100 μm thickness. The decreased thickness ratio of 2212/Ag, about 1:2 as compared with 1:1 of the doctor blade cast tape, is due to the densification of the porous 2212 layer during the previous cold-rolling and laser treatment. Near the silver/2212 interface, and on the top free surface in the fast-scanned sample, large plate-like 2212 grains are well aligned with their *a–b* planes parallel to the tape surface (Fig. 8(a)). However, in contrast with the above X-ray results, the interior regions, especially around some non-superconducting phases, shows poor grain alignment. Moreover, a considerable amount of two blocky non-superconducting phases were found in the interior regions, which were identified as Cu free and Bi free phase by EDX analysis. These second phases interrupt the local grain alignment, and reduce the useful current-carrying cross-section. With a slower scanning rate, these second phases are rarely seen and alignment is further improved (Fig. 8(b)), which is consistent with the X-ray diffraction pattern and the pole-figure results.

4. Summary

In summary,

(1) Bi-2212/Ag composite tapes were prepared by doctor blade casting and then subjected to cold rolling and laser float zone melting to develop a "*c*-axis" texture.

(2) The cold-rolled and sintered tapes show a moderate *c*-axis alignment. However, the microstructure of rolled and sintered samples show the presence of pores and weakly linked grains which would lead to an inferior current-carrying capacity.

(3) Rolling at large reduction ratios per pass, seems

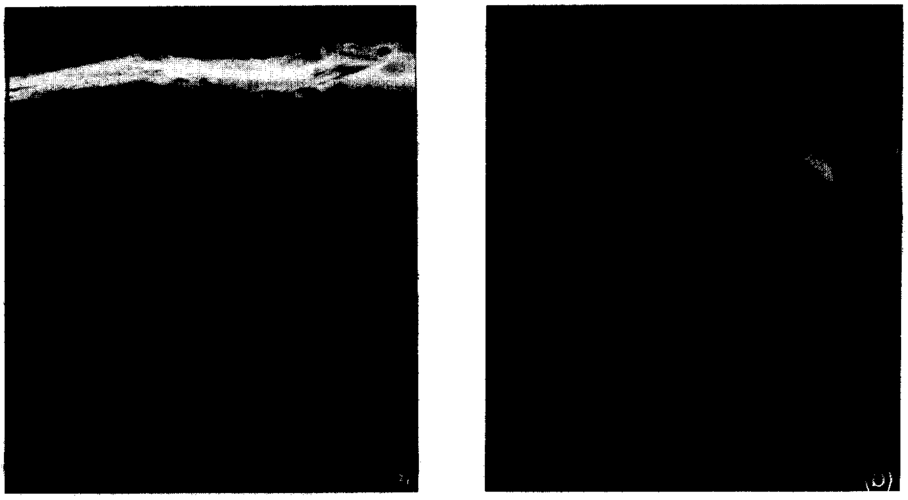

Fig. 8. SEM photographs of polished and etched longitudinal cross-section of laser-treated 2212/Ag tape with a melted zone width of 2.5 mm: (a) scanning rate of 13 mm/h and (b) scanning rate of 10 mm/h.

to be more effective in texture formation than that of low reduction ratio per pass. In both cases, most texturing occurred during the first pass of rolling.

(4) Laser scanned (float zone melting) tapes show a very dense and highly textured microstructure as compared with that of cold-rolled and sintered tapes. X-ray results and SEM micrographs show this *c*-axis alignment improves as the laser scanning rate (i.e., the rate of motion of the molten zone) decreases.

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