ELSEVIER

Physica C 303 (1998) 161–168

PHYSICA C

Processing Bi-2212/Ag thick films under a high magnetic field: on the Bi-2212/Ag interface effect

H.B. Liu, Paulo J. Ferreira *, John B. Vander Sande

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Room 13-5134, Cambridge, MA 02139, USA

Received 2 March 1998; revised 12 May 1998; accepted 14 May 1998

Abstract

Bi-2212/Ag thick films have been melt-processed under the influence of a 10 T magnetic field. With a liquid phase present, the Bi-2212 grain orientation can be controlled by the magnetic field. Under these conditions, the *c*-axis of the Bi-2212 grains produced is always parallel to the applied magnetic field direction and does not depend on the Bi-2212/Ag interface orientation. As a result, a 10 T magnetic field enhances the Bi-2212 grain orientation and texture development for thick films. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Bi-2212; Ag; Magnetic field

1. Introduction

A promising approach for enhancing the critical current density (J_c) of high temperature superconductors is to prepare grain-oriented or *c*-axis-textured material. One way of aligning high-T_c superconductor grains is to utilize a high magnetic field. If a grain has an anisotropic paramagnetic susceptibility in its normal state then, when placed in a magnetic field, the magnetic energy is minimized when the axis of maximum susceptibility is parallel to the magnetic field. The energy associated with this configuration was large enough [1] to align YBCO grains under 9.4 T in epoxy at room temperature. The partial alignment of YBCO powders has also been achieved in isopropanol in a 2 T magnetic field [2]. However, only a limited increase in J_c has been obtained after these processes, since a secondary phase was produced at the grain boundaries during heat treatment [3].

Recently, it was reported that anisotropic grain growth in a Ho–Ba–Cu–O superconductor was introduced under a 1.6 T magnetic field during sintering above 900°C [4]. It was observed that the degree of alignment increased as the magnitude of the magnetic field increased between 0 and 1.6 T for a fixed temperature and processing time. Sarkar and Nicholson [5] also reported that the magnetic field (i.e., 1 T) influences the grain orientation of a YBCO thick film during sintering at 890°C. De Rango et al. [6], Barbut et al. [7] and Bourgault et al. [8] demonstrated that it is possible to prepare textured $YBa_2Cu_3O_7$ ceramic materials by solidification in a 5 T magnetic field. Clots et al. synthesized *c*-axis-oriented magnetically melt-textured $DyBa_2Cu_3O_7$ under a 0.6 T magnetic field [9]. Lewis and Wegmann [10] and Lewis et al. [11] have shown an increase in the

* Corresponding author. Tel.: +1-617-253-6923; Fax: +1-617-268-7874.

0921-4534/98/$19.00
PII S0921-4534(98)00250-0

degree of alignment for YBCO tape-cast films processed under ambient and reduced pO_2 conditions in an applied magnetic field (0–6 T).

For Bi–Sr–Ca–Cu–O 2212/Ag thick films and tapes, *c*-axis alignment of grains introduced by melt-textured growth has been shown [12] to be sufficient to achieve a considerable gain in J_c. It was reported that the textured structure was provided by the flat Bi-2212/Ag interface and liquid phase near the interface. It is claimed that the formation of texture in Bi-2212 partial melt-grown tapes or thick films is dominated by this interface effect and thus, away from the interface, the degree of texture decreases. Consequently, J_c is expected to decrease when the thickness of the tape increases.

Stassen et al. [13] reported an increase in texture of $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8-y}$ under a 0.6 T magnetic induction after sintering at different temperatures. Noudem et al. [14,15], using a thermomagnetic treatment on Bi-2223 pellets, achieved highly textured ceramics in a 8 T magnetic field. Recently, Ma and Wang [16] obtained a high degree of texture in Bi-2223/Ag tapes processed in a 4.5 T magnetic field.

The advantage and potential of processing tapes or thick films by a partial melting method under an elevated magnetic field is, in principle, to produce uniformly textured grains throughout the whole oxide, in contrast to the degree of texture obtained by only melt-textured growth. As a result, J_c should improve above presently achieved values for thicker tapes or films. However, there is the issue as to which effect, the magnetic field or the Ag/Bi-2212 interface, will dominate grain texture development during partial melt-growth of Bi-2212/Ag. In addition, an understanding of the mechanism by which the magnetic field enhances texture may prove of great interest.

In this work, we chose Bi-2212/Ag thick films to verify the effect of the magnetic field on the Bi-2212 grain orientation. By carefully controlling the processing temperature and creating a liquid phase at the Bi-2212/Ag interface, we have successfully controlled the grain orientation of Bi-2212 by a 10 T magnetic field applied during growth. The results will show that the *c*-axis is perpendicular or parallel to the silver substrate depending upon the magnetic field orientation.

2. Experimental procedure

The starting materials were first prepared by solid state reaction. Highly pure (99%) Bi_2O_3, $SrCO_3$, $CaCO_3$, PbO and CuO are weighed according to the normal composition $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_x$. The mixed powders were first reacted at 800°C for 12 h in air. The samples were then ground in an agate mortar and pestle, then pressed into pellets and sintered at 860°C for 24 h. The samples were finally ground into fine particles and the particles were deposited on silver foil in isopropanol. The thick films were dried at 100°C for several hours and heated to 920°C for 5 min, and then quenched to room temperature in air. The quenched amorphous Bi-2212 thick films were processed at 840°C in a vertical furnace which is placed in a 52 mm room temperature bore of a superconducting magnet.

Magnetic fields of up to 10 T are oriented parallel to the long axis of the furnace throughout the annealing cycle. The field was first increased to 10 T, the temperature raised to 840°C, so that the film achieved a partial melted state [17] and then the field held for 10 h.

After the process, the temperature was decreased to room temperature and the magnetic field was reduced to zero. We placed samples in the field in two orientations. In one case, the surface of the film was perpendicular to the magnetic field and in the other case, the surface of the film was parallel to the magnetic field.

Microstructural observations were performed in a JEOL 6320 FEGSEM. Back-scattered electron images were used to produce contrast from the different phases consisting of different elements. The X-ray diffraction was performed in a Rigaku 300 X-Ray diffractometer, using Cu Kα X-ray at 50 kV and 200 mA. Essentially, single-phase 2212 was obtained.

Superconducting transitions were determined from the measurement of Meissner diamagnetic susceptibility as a function of temperature using a Quantum Design superconducting quantum interference device magnetometer (SQUID). The field was first set at 30 Oe and held constant throughout the measurement. The sample was then introduced in the cryostat at $\sim$100 K and cooled to 4.2 K in the magnetic field. The amount of flux expulsion was recorded during the warm-up. Magnetic hysteresis was measured at 4.2 K under zero-field, cooling the sample from room temperature to 4.2 K.

3. Results and discussion

The scanning electron microscopy (SEM) images of the surface and polished cross-section of a sample which was processed at 840°C for 10 h, under a 10 T magnetic field perpendicular to the surface of the film, are shown in Fig. 1. The high degree of texture achieved across the whole thickness is evident. Surface X-ray diffraction patterns of the specimen show strong (001) peaks and very weak (103), (105), (107) and (110) peaks (Fig. 2), a characteristic of samples exhibiting a strong parallel c-axis grain alignment with the Bi-2212/Ag interface.

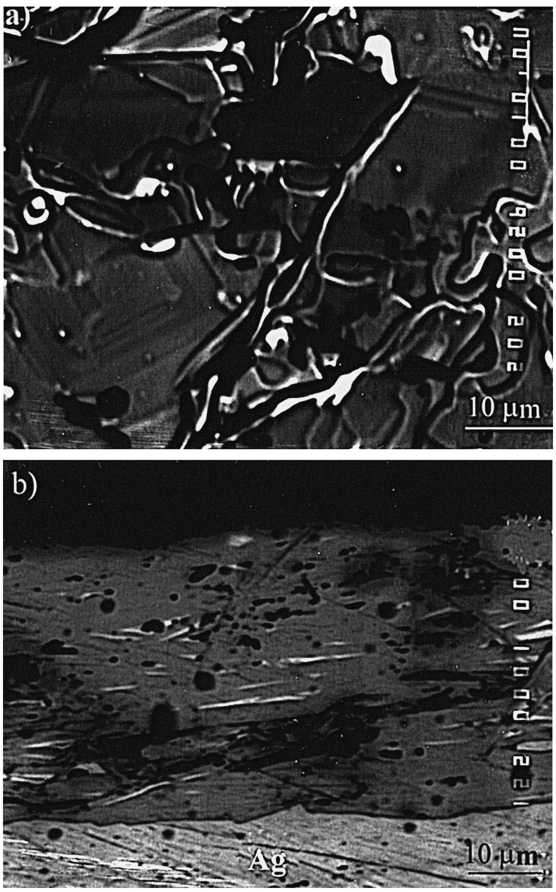

Fig. 1. The SEM images of the sample processed under a 10 T magnetic field for 10 h and with the film surface perpendicular to the processing magnetic field, H_A. (a) Micrograph of the sample's surface. (b) Back-scattering cross-sectional image.

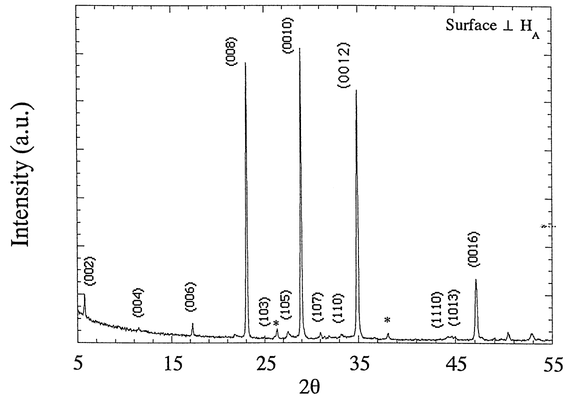

Fig. 2. Surface X-ray diffraction of the sample processed under a 10 T magnetic field and with the surface perpendicular to the processing magnetic field, H_A. (*) shows a small amount of impurity phase.

When the core thickness is ≤ 20 µm, a well-textured structure can be provided by the interface effect alone [12]. However, for thicker melt-textured samples, the degree of alignment is greatly reduced, even at the Bi-2212/Ag interface. For the film shown in Fig. 1, since the thickness is around 60 µm, we claim that the effect caused by the magnetic field is rather significant.

In order to confirm the magnetic field effect alone on the grain orientation, an additional film was processed with the surface parallel to the magnetic field, using the same thermomagnetic process. The SEM images of the polished cross-section and surface of this sample processed under a 10-T magnetic field for 10 h are shown in Fig. 3. In this case, assuming that the c-axis of the grains is the crystallographic direction along which the grains exhibit the lower growth rates, we can argue that across the whole thickness, the c-axis of most grains is parallel to the film surface (Fig. 3a and b). However, the SEM image of the surface of the film reveals that adjacent to the surface, the c-axis of many grains is perpendicular to the Ag substrate (Fig. 3c). A three dimensional schematic view of the grain orientation in the film processed with the surface parallel to the magnetic field is shown in Fig. 4.

This effect, difficult to depict in Fig. 3a and b, is confirmed by the surface X-ray diffraction pattern

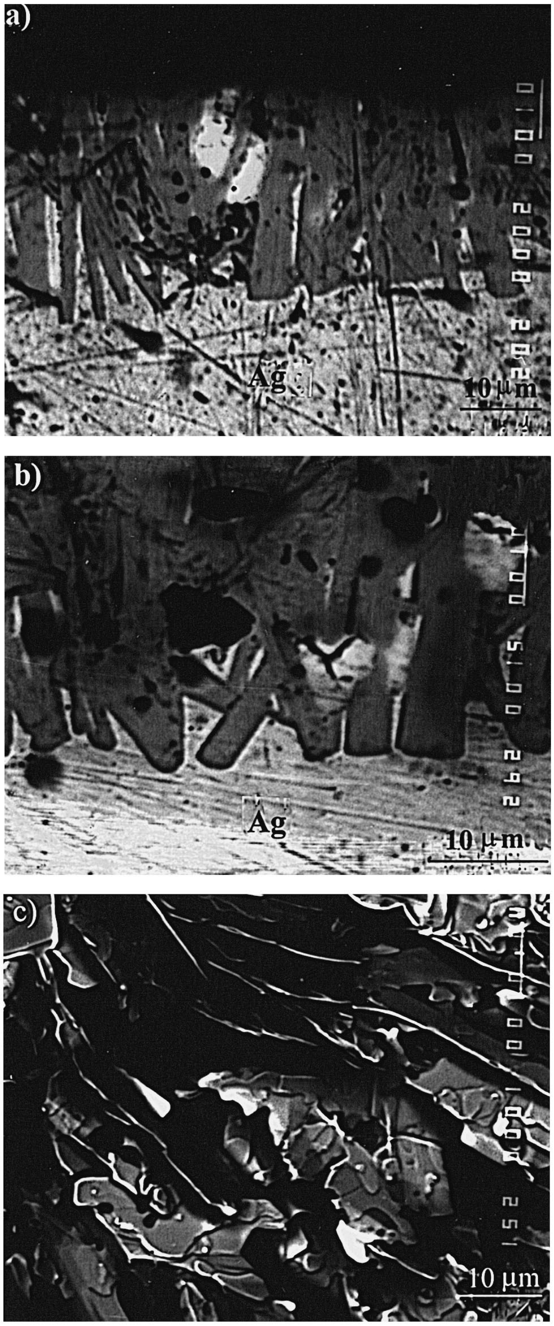

Fig. 3. The SEM images of the sample processed under a 10 T magnetic field for 10 h and with the film surface parallel to the processing magnetic field, H_A. (a) Back-scattering cross-sectional image. (b) Higher magnification of (a). (c) Surface SEM image of the sample.

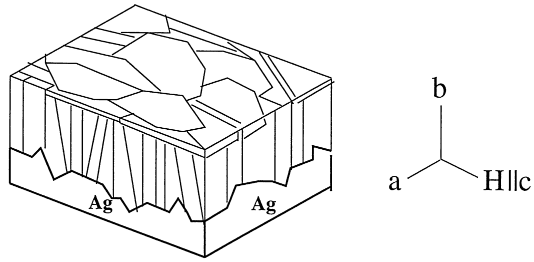

Fig. 4. The 3D schematic view of the grain orientation on the film processed with the surface parallel to the processing magnetic field direction, ***H***. Adjacent to the film surface, the *c*-axis of the grains is perpendicular to the former Bi-2212/Ag interface, whereas below that region, the *c*-axis of the grains is parallel to the interface.

(Fig. 5). In this pattern, strong (001) diffraction peaks appear, which is a characteristic of crystallites with the *c*-axis coinciding with the surface normal. In addition, since the grains with the *c*-axis perpendicular to the surface do not cover the entire surface of the film (Fig. 3c), the intensity of the (103), (105), (107) and (110) diffraction peaks increases and the (200) peak appears in this case. The reason why grains with the *c*-axis direction parallel to the Bi-2212/Ag interface are not observed by the X-ray analysis is due to the shallow penetration of X-rays (a few micrometers). Therefore, only the grains near the free surface can be detected by X-ray diffraction.

The overall anisotropic effect of grain growth is embodied in the measurement of the temperature

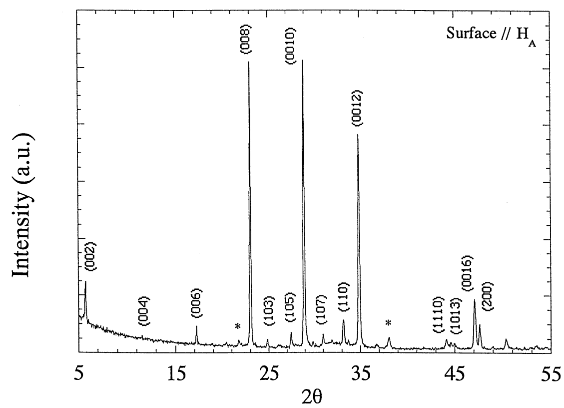

Fig. 5. Surface X-ray diffraction of the sample processed under a 10 T magnetic field and with the surface parallel to the magnetic field, H_A. (∗) shows a small amount of impurity phase.

dependence of the diamagnetic susceptibility (Fig. 6) and magnetic hysteresis at 4.2 K (Fig. 7). In the magnetic measurement, the magnetic field H was applied perpendicular to the film surface. The sample with H parallel to the applied processing magnetic field H_A (the c-axis of most grains is parallel to H) shows a large diamagnetic moment, whereas the sample with $H \perp H_A$ (the c-axis of most grains is perpendicular to H) shows a small diamagnetic moment. This is consistent with the SEM and X-ray diffraction results. For both samples, the superconducting transition temperature is the same (i.e., 76 K), but the ratio of the low-temperature susceptibility for the samples is $\chi(H \| H_A)/\chi(H \perp H_A) = 3.5$. The magnetic hysteresis at 4.2 K shown in Fig. 7 indicates that the orientation of the magnetic field has a significant effect on the grain orientation of the Bi-2212 superconductor grains.

An important question to be asked deals with the way in which the magnetic field induces texture and what is the effect of the Ag/Bi-2212 interface on the thermomagnetic process?

The magnetic driving force for grain alignment is the normal anisotropy energy which is given by $\Delta E = \Delta\chi H_A^2 V/2$, where $\Delta\chi$ is the anisotropic paramagnetic susceptibility, H_A is the applied magnetic field and V is the volume of the grain. The magnetic driving force may affect the nucleation and growth process during solidification, or induce rota-

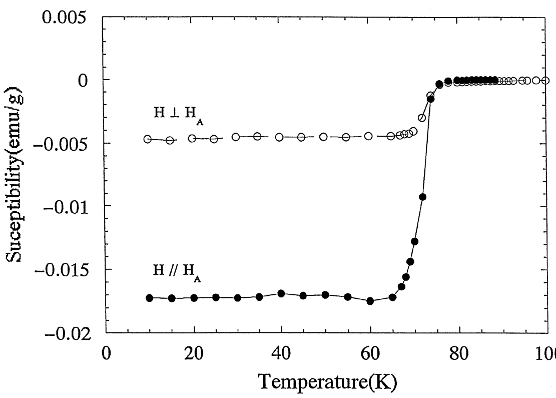

Fig. 6. Temperature dependence of the diamagnetic susceptibility of samples processed under a 10 T magnetic field with the surface perpendicular and parallel to the magnetic field, H_A. The measurement field H is perpendicular to the thick film surface for both samples.

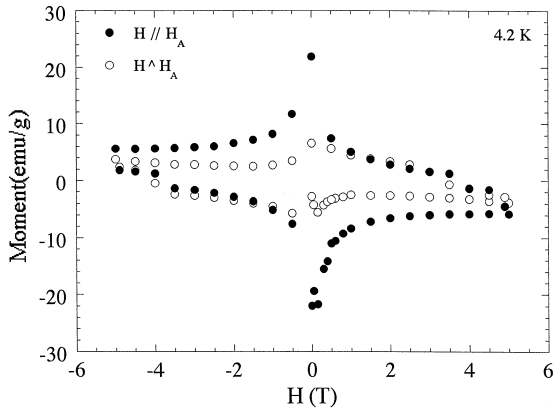

Fig. 7. Magnetic hysteresis at 4.2 K of samples processed under a 10 T magnetic field with surface perpendicular and parallel to the magnetic field, H_A. The measurement field H is perpendicular to the thick film surface for both samples.

tion of the grains if the torque associated with ΔE is sufficiently high to overcome thermal disorder. It is clear that the anisotropy energy depends on the anisotropic paramagnetic susceptibility, magnetic field and volume of the grain. Among these variables, $\Delta\chi$ is temperature-dependent and V is temperature- and time-dependent. As a consequence, the processing time and temperature will affect grain alignment. Thus, for magnetic rotation-induced grain alignment, control of the grain size seems to be rather important. There is a critical volume of a grain, V_c, which corresponds to a magnetic anisotropy energy equal to the thermal disorder energy, kT, i.e., $\Delta\chi H_A^2 V_c/2 = kT$. Thus,

$$V_c = 2kT/H_A^2\Delta\chi.$$

When $V < V_c$, the magnetic field cannot overcome thermal disorder and introduce grain alignment. Once the grain size of Bi-2212 has grown larger than the critical volume, $V > V_c$, during the processing cycle, the magnetic field will tend to rotate the grains. Despite this tendency, there is a mechanical interaction between the grains during the rotation process, which acts strongly against the magnetic energy produced force. However, if there are liquid phases present between the grains, the grains will be more easily oriented by the magnetic field. This is where Pb-doped Bi-2212 and the Ag/Bi-2212 interface play an important role. In the first case, the addition of Pb induces the formation of a liquid phase, which acts as a lubricant between the grains. In the latter case, it has been shown [18] that Ag additions to Bi-2212 cause the formation of an eutectic phase. Thus, near the Ag/Bi-2212 interface, the melting point can be reduced by more than 30 K [17].

The existence of an eutectic reaction due to the presence of Ag, combined with the configuration of Bi-2212 films or tapes, may reveal the mechanism of texture formation during thermomagnetic processing. Any proposed mechanism must explain why grain alignment is improved for thinner films or tapes, why texture is enhanced over larger thicknesses for films processed under a magnetic field and why in thick films or tapes (≥ 20 μm), the region at the Bi-2212/Ag interface is less textured in the absence of a magnetic field [19].

Let us consider the situation depicted in Fig. 8, where a thin (Fig. 8a) and a thick film (Fig. 8b) are represented. Each letter, corresponding to a thickness of 10 μm in the superconductor film, can be associated with a specific Ag composition as a result of Ag diffusion into the superconductor during the processing cycle. This is shown in Fig. 8c where part of a binary Bi-2212/Ag phase diagram is divided into compositional regions representing the superconductor layers A–F. Thus, for a processing temperature

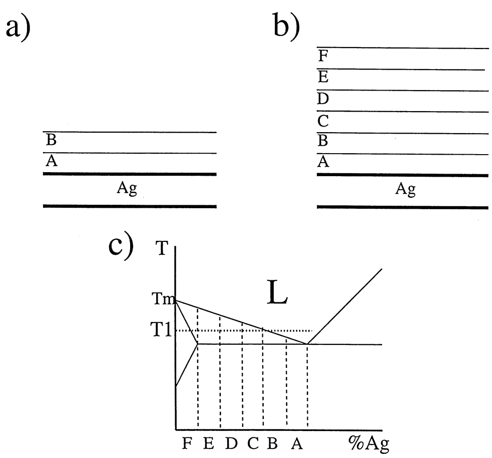

Fig. 8. (a) Schematic of a Bi-2212/Ag thin film divided in compositional layers. (b) Schematic of a Bi-2212/Ag thick film divided in compositional layers. (c) Part of the binary Bi-2212/Ag phase diagram partitioned in various layers. T_1 is the processing temperature and T_m is the melting temperature.

T_1, layers A and B are in a molten state, layers C–E in a partially molten state and layer F in the solid state. In this configuration, the magnetic field-induced grain rotation is mostly taking place within the layers C–E. Within layer F, the strong mechanical interaction between the grains will reduce grain alignment, whereas within layers A–B, there is no material in the solid state.

On this basis, we shall argue that, for the case of the thin film (Fig. 8a), the effect of the magnetic field seems to be related to the nucleation and early growth of grains during the solidification process. In this case, during the early solid growth, the grains are surrounded by a liquid phase and thus, alignment can be achieved more easily. Evidence which supports this mechanism is that when the film surface is parallel to the magnetic field direction, the Bi-2212/Ag interface no longer remains flat and the Ag and the Bi-2212 grains intercalate each other (Fig. 3a and b).

In the case of thick films (Fig. 8b), the mechanism for texture is more complex. During sintering at a temperature, T_1, a gradient in the liquid fraction develops across the entire film. Hence, close to the Bi-2212/Ag interface (layers A and B), where the material is in a molten state, the effect of the magnetic field on grain alignment occurs through its interaction with the nucleation and early growth process, but only during the cooling process. In contrast, away from the interface, where a partially molten state (layers C–E) or even a complete solid state (layer F) remains, the effect of the magnetic field is to immediately induce a rotation of the grains towards a direction where the axis of maximum paramagnetic susceptibility is parallel to the magnetic field. However, for the region where there is no liquid phase, the interaction energy between the grains might be high enough, such that grain rotation in the solid state is hindered.

Some evidence for this mechanism is shown in Figs. 3–5. In this sample, the magnetic field was applied parallel to the film surface during processing. For the region close to the Bi-2212/Ag interface, the *c*-axis of most grains is parallel to the film surface (Fig. 3a–b), i.e., the *c*-axis is parallel to the processing magnetic field, H_A. On the other hand, the grains near the film surface, further away from the interface, still exhibit the *c*-axis perpendicular to

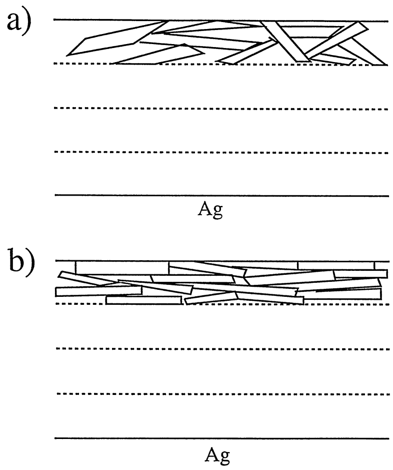

Fig. 9. (a) A schematic view of texture formation in the case where alignment at the top layers did not occur. (b) Case where the presence of a processing magnetic field perpendicular to the film surface enhanced texture over the whole film thickness.

the processing magnetic field (Figs. 3c, 4 and 5). This is a consequence of an increased fraction of solid phase and possibly a free surface effect.

So far, the mechanism described above for thick films has not explained why texture is improved for thicker films or tapes processed under a magnetic field and why in thick films or tapes (≥ 20 μm) influenced by a magnetic field, there is an enhanced texture at the Bi-2212/Ag interface. To answer these questions, one should have in mind what happens during the cooling path.

Thus, to illustrate the situation, let us consider the case where a magnetic field is applied perpendicular to the surface of a thick film or tape with the configuration of Fig. 8b. If the composition at the top layers is such that no apparent grain orientation is obtained under the magnetic field (low processing temperature or high film thickness), the misalignment will be carried throughout the whole film. This is a consequence of the fact that solidification occurs from the top to bottom and therefore, a poor alignment at the top layers complicates the alignment of the next layers (Fig. 9a). On the other hand, if the processing temperature is sufficiently high, or the film thickness is not too large, rotation of the grains under the magnetic field will dominate the texture development at the top layers. This mechanism will enable the packing and alignment of grains throughout the next layers (Fig. 9b) during the cooling process and enhance the degree of texture through the whole body of the superconductor (Fig. 1).

4. Conclusions

A 10 T magnetic field is strong enough to induce a high degree of texture in Bi-2212/Ag thick (≈ 60 μm) films. This is accomplished by grain rotation of Bi-2212 superconductor material under the presence of a liquid phase. In thin films (< 20 μm), the effect of the magnetic field is to influence the nucleation and early growth process. In both thin and thick films, the *c*-axis of Bi-2212 grains is always parallel to the magnetic field direction and does not depend on the Bi-2212/Ag interface orientation. A high magnetic field, in combination with a partial melting process, can thus be used to increase the degree of texture of the whole body of a Bi-2212 superconductor in thick film or tape form.

Acknowledgements

This research is supported by a DOE Grant DE-FG02-85ER 45179. High magnetic field experiments were carried out at Frank Bitter National Magnetic Laboratory at MIT. The authors thank Mr. L. Rubin and D. Lynch for their kind help.

References

[1] D.E. Farrell, B.S. Chandrasekhar, M.R. DeGuire, M.M. Fang, V.G. Kogan, J.R. Clem, D.K. Finnemore, Phys. Rev. B 36 (1987) 4025.
[2] C.P. Ostertag, R.D. Shull, M.D. Vaudin, J.E. Blendell, L.C. Sterns, E.R. Fuller Jr., in: M.F. Yan (Ed.), Ceramic superconductors II, The American Ceramic Society, Weaterville, OH, 1988, p. 332.
[3] F. Chen, B. Zhang, R.S. Markiewicz, B.C. Giessen, Appl. Phys. Lett. 58 (1991) 531.
[4] A. Holloway, R.W. McCallum, S.R. Arrasmith, J. Mater. Res. 8 (1993) 727.
[5] P. Sarkar, P.S. Nicholson, Appl. Phys. Lett. 61 (1992) 492.
[6] P. De Rango, M. Lees, P. Lejay, A. Sulpice, R. Tournier, M. Ingold, P. Germi, M. Pernet, Nature 349 (1991) 770.
[7] J.M. Barbut, M. Barrault, F. Boileua, M. Ingold, D. Bour-

gault, P. De Rango, R. Tournier, Journal de Physique III 4 (11) (1994) 2149.
[8] D. Bourgault, J.M. Barbut, J. Ayache, D. Chateigner, R. Tournier, F.J. Gotor, C. Bahezre, P. Germi, M. Pernet, Physica C 235–240 (1994) 567.
[9] R. Cloots, N. Vandewalle, M. Ausloos, Appl. Phys. Lett. 65 (26) (1994) 3386.
[10] J.A. Lewis, M. Wegmann, Appl. Phys. Lett. 67 (20) (1995) 3028.
[11] J.A. Lewis, A.C. Read, T.K. Holmstrom, IEEE Appl. Super. 7 (2) (1997) 1440.
[12] T.D. Aksenova, P.V. Rratukhin, S.V. Shavkin, V.L. Melnikov, E.V. Antipova, N.E. Khlebova, A.K. Shikov, Physica C 205 (1993) 271.
[13] S. Stassen, R. Cloots, A. Rulmont, F. Gillet, H. Bougrine, P.A. Godelaine, A. Dang, M. Ausloos, Physica C 235–240 (1994) 515.
[14] J.G. Noudem, J. Beille, E. Beaugnon, D. Bourgault, D. Chateigner, P. Germi, M. Pernet, A. Sulpice, R. Tournier, Supercond. Sci. Technol. 8 (1995) 558.
[15] J.G. Noudem, J. Beille, D. Bourgault, D. Chateigner, R. Tournier, Physica C 264 (1996) 325.
[16] Y. Ma, Z. Wang, Physica C 282–287 (1997) 2619.
[17] J. Polonka, M. Xu, Q. Li, A.I. Goldman, D.K. Finnemore, Appl. Phys. Lett. 59 (1991) 3640.
[18] P. Majewski, S. Kaesche, F. Aldinger, Communication T7.7, Materials Research Society Fall Meeting, 1997.
[19] H. Liu, P.J. Ferreira, J.B. Vander Sande, Physica C, submitted.