The influence of elevated magnetic fields on the texture formation of melt-processed Bi-2212

E. Cecchetti, P.J. Ferreira*, J.B. Vander Sande

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Room 13-5114, Cambridge, MA 02139, USA

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Abstract

Melt-processing of BSCCO high-\(T_c\) superconductors (HTS) under an elevated magnetic field is an effective technique for producing superconductors with enhanced critical current. This result is a consequence of the high degree of crystallographic texture achieved in the polycrystalline superconductor processed under a high magnetic field. Possible mechanisms for the orientation of Bi-2212 plate-like crystals under the influence of a magnetic field are analyzed, in particular, the orientation of Bi-2212 superconductor crystals during nucleation, crystal growth and grain growth. In order to understand the relevance of each of these mechanisms, the effect of an applied magnetic field during the different stages of the partial-melt process is studied. Experimental results confirm that most of the alignment is achieved in the early stages of crystal growth.

Keywords: Bi-2212; Magnetic field; Texture

1. Introduction

The use of high-\(T_c\) superconductor oxides (HTS) with high transport critical current density \(J_c\) requires the presence of highly textured superconductor grains in order to minimize grain boundary weak links [1]. One possible route to fabricate HTS polycrystalline materials with a preferred orientation of the superconductor crystals is to melt-process samples under a high magnetic field. In fact, if a HTS grain exhibits an anisotropic paramagnetic susceptibility in its normal state, then when placed in a magnetic field, it minimizes its magnetic energy by aligning its axis of maximum susceptibility parallel to the magnetic field.

Among the different techniques for producing superconductor grain alignment, the application of an elevated magnetic field during the processing of the HTS is appealing because its influence on texture development could be combined with other techniques. Noudem et al. [2] have employed a high magnetic field in association with a hot pressing technique to enhance texture in Bi-2223 samples. Despite some previous encouraging results [3–6], the prospect of using high magnetic fields for extended time portions during superconductor fabrication remains unattractive for large-scale implementation because of limited throughput. Therefore, an important issue for the use of high magnetic fields in processing HTS is to reduce the time of exposure to the
magnetic field without compromising the texture enhancement.

In order to optimize the processing of HTS under a magnetic field, it is important to understand the mechanism by which grain-alignment is achieved. Magnetic field induced grain alignment has been reported both during the solidification from the molten state [5–7] or during the annealing process [8,9], suggesting that the alignment may occur in two ways: (1) rotation of paramagnetic superconductor crystals within a liquid phase, and (2) selective grain growth where grains aligned with their c-axis parallel to the magnetic field preferentially grow at the expense of grains with their c-axis oriented at an angle \( \theta \) with respect to the magnetic field direction.

In a recent paper, Ferreira et al. [10] proposed a model to explain the degree of texture achieved in HTS during melt-processing under an elevated magnetic field. The model suggests that the enhancement in texture is primarily obtained through grain rotation during the early stages of crystal growth from the liquid. During the nucleation of crystals from the melt, when the crystals achieve a critical volume and are still surrounded by a large liquid volume fraction, the magnetic driving force is capable of introducing grain rotation. However, at the later stages of growth, the presence of nearby grains induces grain-to-grain interaction which hinders the magnetic field induced alignment. If the results of this model are valid, a short time exposure to the magnetic field during the initial stages of crystal growth could be sufficient to enhance the texture of HTS materials. Consequently, the opportunity of employing a magnetic field for processing HTS could be reconsidered for large-scale industrial applications.

In order to test the model above [10] and estimate the relevance of the various mechanism of alignment, several experiments were carried out in which a high magnetic field (7 T) was applied during different stages of the Bi-2212/Ag thick film melt-process.

2. Experimental procedure

2.1. Sample preparation

Bi-2212/Ag thick films were prepared with highly pure (99%) \( \text{Bi}_2\text{O}_3 \), \( \text{SrCO}_3 \), \( \text{CaCO}_3 \) and \( \text{CuO} \) weighed according to the nominal composition \( \text{Bi}_{1.875}\text{Sr}_{2.05}\text{Ca}_{0.92}\text{Cu}_{2}\text{O}_x \). The mixed powders were calcinated at 780°C, 800°C and 820°C in air for 12, 12 and 70 h, respectively, with intermediate grinding in an agate mortar and pressed into pellets using an uniaxial and isostatic press (40,000 psi). Subsequently, the samples were ground into fine particles and the particles were dispersed in ethanol. The solution was placed in an ultrasonic bath for 5 min and subsequently poured onto silver ribbons of rectangular shape (2 × 12 mm). Following the evaporation of ethanol at room temperature, the samples were melt-processed in a vertical furnace placed inside a toroidal 52 mm bore superconducting magnet. The final thickness of the films processed was 30 ± 5 μm.

The heat treatment selected was designed to verify the possibility of enhancing the texture formation after a short time application of a magnetic field and to test the relevance of crystal rotation versus selective grain growth to align the superconductor grains. Hence, the heat treatment for the thick films consisted of a partial melting step at 880°C, a first stage of cooling to 860°C at a rate of 1°C/min, a second stage of cooling to 840°C at a rate of 0.1°C/min and an isothermal annealing at 840°C for 40 h (Fig. 1). The temperature of 860°C was chosen because it is below the solidus temperature [11] and consequently crystal rotation is inhibited. In this fashion, we may determine whether the presence of a magnetic field

![Fig. 1. Melt-processing conditions of Bi-2212/Ag thick films in the absence and presence of an elevated magnetic field.](image-url)
could enhance texture formation by the selective grain growth mechanism.

A magnetic field of 7 T oriented parallel to the long axis of the furnace was applied during different stages of the heat treatment (Fig. 1). The films placed inside the furnace had their surface orthogonal to the magnetic field. The sweep rate for the activation/deactivation of the magnetic field was 0.491 T/min. Films labeled A were melt-processed under an applied magnetic field during both stages of cooling (880–860°C and 860–840°C). Films labeled B were melt-processed under an applied magnetic field during the first stage of cooling (880–860°C), so that the magnetic field could play a role during the initial stages of crystal growth. Films labeled C were melt-processed under an applied magnetic field during the slow cooling (860–840°C). In this case, the influence of the magnetic field is expected to be limited to the grain growth regime. Finally, films labeled D were melt-processed in the absence of a magnetic field. Table 1 and Fig. 1 summarize the use of the magnetic field during the different stages of melt-processing. For each process type (A–D) three samples were generated; each specimen was processed independently.

### 2.2. Sample characterization

Surface X-ray diffraction (XRD) can be used to determine the degree of texture in a polycrystalline material. A quantitative measure of c-axis orientation can be obtained from the XRD spectra by using the Lotgering factor ($F$) [12], which can be calculated as follows

$$F = \frac{(P - P_0)}{(1 - P_0)},$$

where $P = \sum_{(00l)} I_{(00l)}/\sum_{(hkl)} I_{(hkl)}$ is the sum of XRD peak height intensities for all (00l) reflections divided by the sum of all intensities ($hkl$) in the textured specimen, $P_0$ is the XRD peak height intensity ratio of a randomly oriented specimen. The factor $F$ varies from 0 (random) to 1 (completely-orientation). The XRD work was performed in a Rigaku 3000 X-Ray diffractometer, using CuKa X-ray radiation at 60 KV and 300 mA. Microstructural observations were performed in a JEOL 6320 FEGSEM using an accelerating voltage of 10 keV. Backscattered electron images were used to produce contrast from the different phases consisting of different elements. The $J_c$ was evaluated using a transport current technique with the four-probe DC method. A criterion of 1 μV/cm was used to determine $J_c$.

### 3. Results and discussion

Surface XRD patterns of film A (Fig. 2a), B (Fig. 2b), C (Fig. 2c), and D (Fig. 2d) show strong (00l) peaks, very weak (2210), (2214) peaks and a few peaks corresponding to impurity phases. This implies that all the melt-processed Bi-2212 thick films exhibit a high degree of texture since the intense (00l) peaks shown by the surface XRD pattern are a characteristic of films exhibiting a strong c-axis grain alignment orthogonal to the film surface. A difference in the position and intensity of X-ray peaks corresponding to the presence of impurities is evident. This variation is likely due to small fluctuations in temperature and humidity (one degree temperature difference and minor changes in the atmospheric pressure are capable of introducing visible differences in the X-ray spectra). However, these minor changes in impurity content do not lead to changes in the critical current density observed as confirmed by comparing samples A and C. In the latter specimen, the X-ray spectrum shows a small impurity peak whereas sample A exhibits a larger number of these peaks. Notwithstanding, sample A exhibits a larger critical current density than sample C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>880–860°C (20 min)</th>
<th>860–840°C (200 min)</th>
<th>840°C (40 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>Selective grain rotation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetic field</td>
<td>Magnetic field</td>
<td>Magnetic field</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>on</td>
<td>on</td>
<td>off</td>
</tr>
<tr>
<td>B</td>
<td>on</td>
<td>off</td>
<td>off</td>
</tr>
<tr>
<td>C</td>
<td>off</td>
<td>on</td>
<td>off</td>
</tr>
<tr>
<td>D</td>
<td>off</td>
<td>off</td>
<td>off</td>
</tr>
</tbody>
</table>
The presence of impurity phases is indicated by the symbol . In order to differentiate the degree of texture among films A, B, C and D, the Lotgering factor \( F \) was calculated, as shown in Fig. 3. The average value of \( F \) was calculated on the basis of three samples. All the samples exhibit a high level of texture \((F > 0.94)\). However, the highest value for \( F \) was obtained for film type A, in which both crystal rotation and selective grain growth was expected to occur. The application of a magnetic field solely during the first stage of cooling (film type B), where crystal rotation can occur, seems to be significantly more effective in enhancing the texture than the application of a field during grain growth (film type C).

SEM backscattered images of polished cross-sections of films A, B, C and D are shown in Fig. 4. The films consist of Bi-2212 with small amounts of impurity phases, mainly Bi-2201 (white phase) and the Bi-free 014 × 24-phase (black phase) [13]. The grains appear to be aligned with the crystallographic \( c \)-axis (the direction of lowest growth rate) orthogonal to the surface through the entire thickness of the films.

In Fig. 5, the transport critical current density of the films, measured at liquid helium temperature, are plotted as a function of the processing conditions. The maximum value in \( J_c \) occurs in films where the magnetic field was present during the entire cooling process (film type A). The application of a magnetic field during the solidification from the molten state (film type B) results in higher \( J_c \)'s than film type C.
Fig. 4. Backscattered electron images of Bi-2212/Ag cross-sections melt-processed under a 7 T magnetic field during both cooling stages (880–840°C, Film A) (A), during the first stage of cooling (880–860°C, Film B) (B), during the second stage of cooling (860–840°C, Film C) (C), and in the absence of a magnetic field (Film D) (D).

where the magnetic field is present during grain growth. The process in the absence of a magnetic field (film type D) exhibits the lowest $J_c$, although the value is very close (within the standard deviation) to the critical current density obtained for films C. The improvement in $J_c$ for thick films A and B is a consequence of the enhancement in the degree of texture, which is confirmed by the Lotgering factors shown in Fig. 3. The difference in texture improvement is difficult to distinguish from the SEM micrographs (Fig. 4), due to the high degree of alignment obtained in all samples.

These results confirm that a magnetic field is more effective in enhancing the texture development of Bi-2212 thick films during the solidification regime than during the grain growth process. In this case, although the application of a magnetic field was limited to 20 min, a $J_c$ enhancement of approximately 50% was achieved in comparison with samples processed in the absence of a magnetic field. On the other hand, the application of a 7 T magnetic field during the grain growth process only improved the critical current density by less than 10%. Hence, it can be argued that the modest improvement in critical current density shown by samples C (magnetic field applied during grain growth) may be
explained by a statistical fluctuation, since their $J_c$ value is within one standard deviation of the $J_c$ value for samples D (absence of a magnetic field). However, the variance between the critical current density of films A and B, for which the only difference in the processing procedure was the absence of a magnetic field during grain growth in film type B, corroborates the hypothesis that texture formation can only be weakly enhanced during grain growth. This result could have been expected, since several research works have reported a $J_c$ improvement in samples sintered for long times ($> 10$ h) under a high magnetic field, i.e. in the grain growth regime [8,9]. This conclusion is in agreement with the analysis developed by Ferreira et al. [10]. After deriving the driving force for the grain growth of a grain aligned with the field, a semi-empirical analysis showed that high intensities and long time exposures are required for the magnetic field to be effective in enhancing texture during grain growth.

The current experiments have demonstrated that a magnetic field can be effective in improving $J_c$ during the early stages of solidification from the molten state. Two alignment mechanisms seem to be possible during this stage, namely: preferred nucleation and crystal rotation. Preferred nucleation may occur since the presence of a magnetic field lowers the energy for nucleation for nuclei aligned with their $c$-axis parallel to the magnetic field. However, it has been shown [10] that the effect of an elevated magnetic field on the nucleation rate is inconsequential. On the other hand, crystal rotation may occur because a superconductor crystal immersed in a liquid, under a magnetic field, experiences a torque, in the form

$$\tau = 1/2(\Delta \chi H^2 V \cos \theta \sin \theta),$$

(2)

where $\Delta \chi$ is the difference in the volume susceptibility of a crystal, $H$ is the magnetic field, $V$ is the volume of the crystal, and $\theta$ is the angle between the magnetic field and the $c$-axis of the crystal. The torque tends to cause an angular rotation of the $c$-axis of the crystal in the direction of the applied field. Consequently, the torque will tend to increase the texture of the superconductor. Since preferred nucleation is negligible, crystal rotation under a magnetic field must be the mechanism leading to the crystal alignment. It can be noticed (Eq. 2) that the torque $\tau$ is proportional to the volume of the crystal, thus it is expected that larger grains are more easily oriented. However other factors may hinder the orientation induced by the torque $\tau$, such as thermal agitation, impingement with other crystals, the presence of impurity phases and the viscosity of the surrounding liquid.

Assuming that a high magnetic field enhances the texture through crystal rotation in the early stage of solidification, a question regarding the exposure time limit to a high magnetic field for improving efficiently the texture in Bi-2212 arises. Thus, it is important to keep in mind that the cooling rate cannot be efficiently decreased below a certain value (close to 1°C/min) since with a faster cooling, the amount of secondary phases, detrimental for $J_c$, increases drastically [14]. Consequently, since crystal rotation occurs in a certain interval of time depending on the cooling rate, it may follow that the exposure time cannot be efficiently reduced below 10–20 min.

4. Conclusions

The degree of texture and transport critical current density in Bi-2212 thick films can be enhanced by a short time application (20 min) of a magnetic field during the early stages of solidification. The mechanism behind this effect consists of a grain rotation during the early stages of crystal growth. A mechanism of selective grain growth under a high magnetic field may enhance the texture formation and transport critical current density in later stages, but to a much lesser extent.

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References


