

TEXTURE DEVELOPMENT IN SUPERCONDUCTING OXIDE/AG THICK FILMS
IN THE PRESENCE OF A MAGNETIC FIELD (0-7 TESLA)

by

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ABSTRACT

Various mechanisms for texture formation in Bi-2212/Ag thick films processed in the absence and presence of a high magnetic field have been analyzed.

In the absence of a high magnetic field during the melt-processing of BSCCO samples, interfacial energy effects determine the degree of texture for these high-T_c superconductor. Scanning electron microscopy analyses of different BSCCO systems corroborates the hypothesis that the interfacial energy of a BSCCO crystal is minimized when the planar surface of the crystal is in contact with silver (substrate or added particle) or an impurity phase. As a consequence, a flat silver surface may enhance the alignment of superconductor grains close to the Bi-2212/Ag interface, whereas impurity phases and silver particles of a random shape have a deleterious influence on texture formation.

The presence of a high magnetic field may improve the critical current density of Bi-2212/Ag thick films, by enhancing the texture formation of the superconductor grains. Three models for the alignment formation under a high magnetic field have been proposed, namely, preferred nucleation, crystal rotation and selective grain growth. In order to understand the relevance of each mechanism, the effect of an applied magnetic field during different stages of the partial-melt process is studied. Experimental results show that most of the alignment under a high magnetic field is achieved in the early stages of solidification when crystal rotation may occur. In this case, the use of a high magnetic field for a short time may lead to a considerable improvement in the critical current density.

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Introduction

Since the first report of superconductivity in the BSCCO system [1], an enormous quantity of material has been reported on the Bi-system. Tremendous advance has been already made and superconducting wires, made with this brittle material have been employed in the construction of motor, generators, alternators and power transmission cables with superior performance [2].

The material science challenges of these complicated systems are to understand the interrelationships between the chemistry, the processing, and the resulting microstructure and electric properties so that the technology can advance from the present promising state of research to the large applications of BSCCO superconductors. In order to achieve this goal, the microstructure of the superconductor should be single phase with highly aligned grains.

In this work, texture development of BSCCO superconductors has been analyzed. The structure of the thesis consists of two manuscripts for journal publication, sandwiched by a global introduction and a general conclusion.

In the first manuscript, the relevance of interfacial energy effects in the melt-processing of BSCCO superconductors, particularly the Bi-2212 phase, has been studied. The results of a model have been corroborated by scanning electron microscopy observations of the BSCCO microstructure. These results have important consequences on the texture formation of polycrystalline BSCCO superconductor.

In the second manuscript, the use of a magnetic field to texture a high temperature superconductor has been analyzed. Specifically experiments have helped to clarify the dynamics of the superconductor grain alignment under a high magnetic field.

Encouraging results on the influence of a short time exposure to the magnetic field during the melt-processing of Bi-2212/Ag thick films may have important consequence for the large scale implementation of this technique.

Reference

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CHAPTER 1

A Model for Texture Development in BSCCO High-Tc Superconductors

Abstract: Textured BSCCO superconductors are studied and the various mechanisms for alignment of BSCCO grains addressed. To date, surface energy effects leading to texture development of BSCCO superconductors have been considered only with respect to the free surface of melt-processed Bi-2212 thick films. However, these previous efforts have not included the surface interactions between BSCCO crystals and other solid surfaces present in the BSCCO system. In the present work, a model based on an interfacial energy relation is proposed. In order to verify the model, a variety of experiments have been performed. The observation of the microstructure in different BSCCO samples corroborates this model. The following discussion offers a plausible explanation for the various observed phenomena during the partial melt process. During the early stages of solidification, when the peritectic liquid is abundant, BSCCO crystals are rather mobile, facilitating their contact and interaction. As a result, if a crystal has its wide planar c-surface in contact with a foreign surface (e.g. silver substrate, secondary phases, free surface or another BSCCO crystal), it can minimize its surface energy and likely adhere to that surface. This mechanism, applied to a system with planar constraints like a 2212/Ag film, will result in a textured sample, depending on the thickness of the superconducting layer. In a bulk sample however, BSCCO crystals may only minimize their surface energy by adhering to other BSCCO crystals, which consequently will form clusters of locally aligned crystals, i.e. colonies, with no long-range texture. In this fashion, we may also address the role of silver in promoting texture development in BSCCO superconductors.

1. Introduction

Large critical current densities (J_c)'s are required for many proposed applications of high- T_c superconductors (HTS's), such as wires, solenoids and magnets [1]. Although high critical current densities (J_c 's) have been obtained in HTS single crystals [2], the large-scale application of polycrystalline HTS is limited mainly by the poor alignment of superconducting grains that results in grain boundary weak links with low values of J_c [Bourdillon].

Of the three major families of HTS, Y-Ba-Cu-O (YBCO), Bi-Sr-Ca-Cu-O (BSSCO), and Tl-Ba-Ca-Cu-O (TBCCO), the best wires produced have been made of BSSCO material [3]. Three superconducting phases are known in this system: Bi-2201 ($T_c \sim 20\text{K}$), Bi-2212 ($T_c \sim 90\text{K}$) and Bi-2223 ($T_c \sim 110\text{K}$). The microstructure of any of these three phases consists typically of BSSCO platelets oriented parallel to the a-b planes of the lattice (Fig. 1).

Although significant results in the fabrication of BSSCO thick films and tapes have been obtained ($J_c \sim 20\text{kA/cm}^2$ at 77K [4]), further improvements are required in order to render these compounds suitable for large-scale applications. Hence, it is important to fully understand the mechanisms that lead to a highly textured microstructure.

In Bi-2223 it is difficult to align well the superconducting grains, because of the complex formation mechanism of the Bi-2223 superconductor phase, whereas in the fabrication process of Bi-2212, the sequence of partial melting and subsequent slow solidification

(Fig. 2) is effective in obtaining a highly oriented c-axis grain microstructure. The interest in Bi-2212-based tapes or thick films is a consequence of their possible use in superconducting magnets at high magnetic fields and liquid helium temperatures [5].

Thus far, four mechanisms for the texture formation in melt-processed Bi-2212 have been suggested, namely a) heterogeneous nucleation on planar interfaces [6], b) buoyancy effects [3], c) opportunistic growth [7] and d) anisotropic grain growth [8].

The mechanism of heterogeneous nucleation on planar interfaces is based on a comparison between Bi-2212 thick films or tapes with varying thicknesses, for which the degree of texture decreased with increasing thickness [6]. It has been proposed that texturing proceeds from the sample surface and from the silver substrate outward [6]. An implicit assumption of this model is that during the cooling process from the melt, heterogeneous nucleation on the free surface and/or the Ag/BSCCO interface governs the nucleation process (Fig. 3.a). Since the free surface and the Ag/BSCCO interface are to some extent flat, they constitute a good template for growing superconductor crystals aligned with their c-axis perpendicular to the Ag/BSCCO interface (Fig. 3.b). As the solidification proceeds from the interface outward, the alignment of the c-axis of the superconductor grains decreases far from the interfaces, leading to the result that thick films exhibit a low degree of texture (Fig. 3.c) [3].

The suggestion of buoyancy effects has its origin in in-situ high temperature microscopy observation of melting and crystal growth of Bi-2212 thick films. Using the former technique, Hasebe et al. [9] observed that Bi-2212 platelets were floating on the surface

of partially molten thick films. In addition, XRD spectra of these samples, quenched after a gradual cooling from 870 C, showed very strong $00l$ reflection lines of the 2212 phase, confirming that the c-axis of the grains close to the free surface was perpendicular to the substrate. Hasebe et al. [9] concluded that the texture of the 2212 phase was strongly dependent on the free surface of the solution, and not on the interface between the solution and the substrate. Hence, it has been argued [3] that the mechanism for texture formation could reside on a density difference between the peritectic liquid and the superconductor crystals. The liquid being denser, 2212 crystals could flow and float to the top, where they could align if they encounter a horizontal surface, (Fig. 4.a-b)

After studying Bi-2212/Ag tapes prepared by the “powder in tube” method and the partial melt process, Aksenova et al. [7] proposed the so-called opportunistic grain growth model for texture formation. The opportunistic grain growth model or unimpeded grain growth model is based on the following suppositions: 1) high anisotropy of crystal-growth rate, 2) quasi-two-dimensional crystallization space (i.e. the tapes or films), and 3) wide separation distance between grains at the beginning of the crystal growth process. Preferential alignment may occur when the environment in which the grains are growing is geometrically constrained and the morphology of the grains favors grain growth in certain directions. Grains that are growing in directions free of constraints grow larger than grains oriented in directions limited by the constraints of the system, such as the silver substrate. Hence, for plate-shape 2212 grains, the growth of grains oriented with their ab-axis parallel to the silver interface should be favorable with respect to the other

orientations. This mechanism results in an enhancement in c-axis grain alignment perpendicular to the interface.

Through SEM micrographs of Bi-2212/Ag thick films quenched during the various stages of melt-processing, Lang et al. [8] showed that various reactions may occur when the growth of a Bi-2212 grain is hindered by an obstacle. In particular, Bi-2212 grains can stop growing, change their direction or even grow through the obstacle. A mechanism of texture development based on anisotropic crystal growth which allows small grains to turn themselves into a favorable orientation was consequently proposed [8]. Since crystal growth in the c-direction is much slower than in the ab-planes, when a grain encounters an obstacle (Fig. 5.a-b), it is very unlikely that the growth in the ab-directions ceases and growth proceeds solely in the slow c-direction. In order to continue to grow the grain may bend (Fig. 5.c). However the bending is accomplished by distortions at the atomic scale. This results in a driving force that favors the grains remaining planar. This force can turn the platelet in an orientation parallel to the obstacle as long as the platelet is small enough and other grains do not hinder the movement (Fig. 5.d). This leads to a collective alignment of neighboring grains [8].

In spite of these arguments, these models give an incomplete explanation of the various phenomena observed during the melt-process of Bi-2212. The major limitations of these models are summarized by the following observations.

With respect to the mechanism of heterogeneous nucleation, SEM micrographs of samples quenched during the early stages of nucleation [3,8] excluded the fact that

nucleation may occur preferentially at the interfaces or at the free surface. Concerning the buoyancy effect, Hellstrom et al. [3,10] performed some experiments in which the samples were partially melt-processed in different orientations with respect to the direction of the gravity force. No significant change in texture was noted [3,10]. This observation implies that the buoyancy of 2212 is not a major factor inducing alignment. In the opportunistic grain growth model [7], computer simulations [8] have shown that the effect of this mechanism is too weak to explain the high degree of texture achieved in melt-processed samples. Finally, for the model based on anisotropic grain growth a direct observation has not yet been made. However, the observed formation of Bi-2212 grains in contact with each other and having their c-axes parallel with each other cannot be justified, solely on the basis of this model.

Hence, even if mechanisms for the formation of texture in melt-processed Bi-2212 thick films and tapes have been proposed, no model which can explain all the observed microstructural features has been developed.

In the following sections we present a model based on interfacial energy relations. In order to prove the validity of the assumptions used in this model, some experiments have been performed. Subsequently, the consequences of the model on the texture development are discussed.

2. Experimental Procedure

In order to verify the interfacial energy relations we will assume in Sect.3, three different experiments have been designed.

a) *Bi-2212/Ag thick film presenting irregularities on the silver substrate*

Bi-2212/Ag thick films were prepared with highly pure (99%) Bi_2O_3 , SrCO_3 , CaCO_3 and CuO weighed according to the nominal composition $\text{Bi}_{2.15}\text{Sr}_{2.05}\text{Ca}_{0.95}\text{Cu}_2\text{O}_x$. The mixed powders were first reacted at 800°C for 12 hours in air. The samples were then ground in an agate mortar and pestle, pressed into pellets and sintered at 860°C for 24 hours. The samples were finally ground into fine particles and the particles were deposited on silver foil in isopropanol. Previously, some grooves (1-3 μm deep) were created on a silver substrate with the use of a stainless steel blade. The composite was finally melt processed, following the diagram in Fig.2.

b) *Bi-2212 pellet*

Bi-2212 pellets were prepared with highly pure (99.9%) Bi_2O_3 , SrCO_3 , CaCO_3 , PbO and CuO weighed according to the nominal composition $\text{Bi}_{2.15}\text{Sr}_{2.05}\text{Ca}_{0.95}\text{Cu}_2\text{O}_x$. The initial powders were mixed and ground, placed into a ball mill with ethyl alcohol and subsequently ground for several hours. The alcohol was then evaporated. The remaining powder was then submitted to a calcination at 800°C for 24 hours. Following the calcination procedure, $\frac{1}{4}$ inch diameter pellets were made and subjected to an iso-press under 34,000 psi. The pellet was finally melt processed, following the diagram in Fig.2.

c) *Bi-2223 + 5wt% Ag pellet*

Bi-2223 pellets were prepared with highly pure (99.9%) Bi_2O_3 , SrCO_3 , CaCO_3 , PbO and CuO weighed according to the nominal composition $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{1.9}\text{Cu}_{3.09}\text{O}_x$. The initial powders were mixed and ground, placed into a ball mill with ethyl alcohol and subsequently ground for several hours. The alcohol was then evaporated. The remaining powder was then submitted to a calcination at 810 C for 12 hours. Following the calcination procedure, $\frac{1}{4}$ inch diameter pellets were made and subjected to an iso-press under 34,000 psi.

The pressed pellets were pre-heated twice before the sintering cycle. The pre-heat treatments consisted of a slow heating rate (1C/min), in air, in the range 600-800 C. Subsequently, 5wt% of silver particles with an average size of 0.1 μm were introduced into the pre-treated samples which were sintered at 850 for 24 hours followed by a slow cooling (10C/hour) under a partial pressure of oxygen (PO_2) of 0.075 atm.

Microstructural observations were performed in a JEOL 6320 FEGSEM. Backscattered electron images were used to produce contrast from the different phases.

3. Results

3.1. Results from the Model.

Let us begin by considering that the interfacial tension between the surface parallel to the a,b plane (c surface) of a superconductor crystal (Fig.1) and a foreign surface is less than

the sum of the interfacial tension between the \underline{c} surface of a superconductor crystal and the peritectic liquid, and the interfacial tension between the distinct surface and the liquid.

In a mathematical form this assumption can be formulated as follows:

$$\gamma_{\text{BSCCO/S}}(\underline{c}) < \gamma_{\text{BSCCO/L}}(\underline{c}) + \gamma_{\text{S/L}} \quad (1)$$

where \underline{c} is the vector orthogonal to the \underline{c} surface, $\gamma_{2212/\text{S}}(\underline{c})$ is the interfacial tension between the foreign surface and the \underline{c} BSCCO surface, $\gamma_{2212/\text{L}}(\underline{c})$ is the interfacial tension of the \underline{c} surface of a BSCCO crystal in the peritectic liquid and $\gamma_{\text{S/L}}$ is the interfacial tension between the foreign surface and the peritectic liquid.

Foreign surfaces in Eq.1 can be surfaces with which a BSCCO crystal could come in contact, such as the silver substrate, impurity phase particles, pores, other BSCCO platelets and the free surface.

Let us examine the implications of Eq.1 on 1) the nucleation and 2) crystal growth processes.

3.1.1 Nucleation

Consider the heterogeneous nucleation of BSCCO on silver, secondary phases and/or on the free surface. As an example, let us consider silver, for which the excess energy associated with the formation of a superconductor embryo can be written as:

$$\Delta G = V\Delta G + S_{BSCCO/Ag} \gamma_{BSCCO/Ag}(\underline{c}) - S_{BSCCO/L} \gamma_{BSCCO/L}(\underline{c}) - S_{Ag/L} \gamma_{Ag/L} \quad (3)$$

where V is the volume of the BSCCO embryo, ΔG_V is the change in the chemical free energy per unit volume of the solid; $S_{BSCCO,Ag}$, $S_{BSCCO,L}$ and $S_{Ag,L}$ are the interfacial areas between the silver and the embryo, the peritectic liquid and the embryo, and the silver and the liquid, respectively. Since BSCCO crystals have a platelet shape, we may reasonably approximate the shape of the superconductor embryo with a spherical cap, with the superconductor c -axis orthogonal to the BSCCO/Ag interface (Fig. 6). In this case the activation energy barrier against heterogeneous nucleation is given by [11]:

$$\Delta G_{Het}^* = \Delta G_{Hom}^* (2+k)(1-k)^2 / 4 \quad , \quad (4)$$

where ΔG_{Het}^* is the activation energy barrier against heterogeneous nucleation, ΔG_{Hom}^* is the activation energy barrier against homogeneous nucleation and k is a parameter given by

$$k = \frac{\gamma_{BSCCO,Ag}(\underline{n}) - \gamma_{Ag,L}}{\gamma_{BSCCO,L}(\underline{n})} \quad (5)$$

where \underline{n} is a vector normal to the surface. Eq.1 implies that $k < 1$, which subsequently gives

$$\Delta G_{Het}^* < \Delta G_{Hom}^* \quad (6)$$

Thus, the activation energy barrier against heterogeneous nucleation is expected to be significantly lower than the activation energy barrier against homogeneous nucleation.

3.1.2 Crystal Growth

After the nucleation of superconducting embryos, the growth of BSCCO platelet crystals occurs (Fig. 2). Let us analyze the implications of Eq.1 in the event of a superconducting crystal coming in contact with a foreign surface.

Considering the case where the planar surface of a BSCCO crystal and a surface S contact each other (Fig.7 I). If A_I is the area of contact, the change in surface free energy of the system can be written as:

$$\Delta E = A_I \gamma_{\text{BSCCO,S}(\underline{c})} - A_I \gamma_{\text{BSCCO,L}(\underline{c})} - A_I \gamma_{\text{S,L}} < 0 \quad (7)$$

In other words, Eq.7 shows that the crystal minimizes its interfacial energy, when the two surfaces are in contact. Note that the gain in energy is proportional to the area of contact (Eq.7). If the surface of the crystal in contact with the substrate is not the \underline{c} surface (Fig.7 II, III), the area of contact will be considerably smaller (typical aspect ratios for BSCCO crystals are close to 20) and so the gain in energy associated with the contact can be expressed as:

$$\Delta E_{\text{BSCCO,S}(\underline{c})} < \Delta E_{\text{BSCCO,S}(\underline{n})} , \quad \underline{n} \neq \underline{c} , \quad (8)$$

where $\Delta E_{\text{BSCCO,S}}(\underline{n})$ is the energy gain when a BSCCO crystal surface with normal vector \underline{n} is in contact with a solid surface. Consequently, in this case, the contact is less stable and the superconducting crystal will more likely move away.

An alternative way of interpreting the interfacial energy Eq.1 is by considering the liquid wetting angle, θ . In this formulation Eq.1 can be rewritten as:

$$\gamma_{\text{BSCCO,S}}(\underline{c}) = \gamma_{\text{BSCCO,L}}(\underline{c}) \cdot \cos\theta + \gamma_{\text{S,L}}, \quad (9)$$

where the wetting angle of the liquid, θ , must be greater than zero (partial wetting). This situation is schematically shown in Fig. 8.a. When θ is greater than zero, a BSCCO crystal in contact with a foreign surface and satisfying Eq.9 is trapped on the surface. On the other hand (Fig. 8.b) if θ is equal to zero, complete wetting of the surface by the peritectic liquid should occur and thus the superconductor crystal should be pushed away from the surface because the liquid film is present between the superconductor crystal and the foreign surface.

3.2. Experimental Results

In order to verify the previous model, it is necessary to investigate the microstructure of BSCCO samples processed under different conditions. In fact the final microstructure is affected by the thermodynamics of the surfaces. In particular, if a foreign surface S satisfies Eq.1, the BSCCO grains in contact with the surface S are expected preferentially with their \underline{c} surface parallel to S (see Sect.3.1.2.). Consequently, the observation of the microstructure of BSCCO samples may corroborate or contradict Eq.1. The samples

considered have been designed specifically to test Eq.1 in the case of contact between a BSCCO crystal and an impurity phase or silver. Both Bi-2212 and Bi-2223 were considered. However, their interfacial energy relations are expected to be quite similar, since the only difference between the two crystals resides in the extra CuO_2 plane of the Bi-2223 crystal.

a) *Bi-2212/impurity phase*

A melt-processed Bi-2212 pellet was prepared with the purpose of studying the interfacial tension between Bi-2212 grains and impurity phases. A pellet was preferred on a thick film, for this case, because the microstructure observable inside a bulk sample is less influenced by the boundaries of the sample. The final microstructure consists mainly of Bi-2212 and a few impurity phases, particularly Bi-2201 and the Bi-free 014×24 -phase. Fig.9 shows a partial cross-section of a Bi-2212 pellet, in which two black impurity particle (the Bi-free phase) are entrapped by Bi-2212 grains. The superconductor grains are in contact preferentially with the c surface or, in other words, with their ab -planes parallel to the surface.

b) *Bi-2212/silver substrate*

In order to investigate the validity of Eq.1 for the Bi-2212/silver interface, we have considered a Bi-2212/Ag thick film in which, the silver substrate was previously treated in order to present irregularities on its surface. The final thickness of the film was close to $40 \mu\text{m}$ and consisted of Bi-2212 (dark gray phase) and Bi-2201 (light gray phase). The conversion from Bi-2201 to Bi-2212 was deliberately modest, since the contrast between Bi-2201 and Bi-2212 phases makes it easier to distinguish the

orientation of the grains. In Fig. 10, a cross-section of a melt-processed Bi-2212/Ag thick film is shown where the silver ribbon exhibits two bumps of similar depth. In addition to the alignment along the Bi-2212 longitudinal direction, we can observe that the presence of bumps acts as a template for the Bi-2212 grains. Micro-cracks are also evident on the region of higher curvature (white arrows), probably a consequence of a fast cooling (fast thermal contraction) and high stresses present in that region. In fact, high stresses must be present in the region of the high curvature region because the bending of the grain must be compensated by a high distortion of the atomic bonds.

c) *Bi-2223/silver particle*

A Bi-2223 pellet processed with an addition of 5wt% of silver particles, has been observed to verify the validity of Eq.1 for the Bi-2223/silver interface. At the end of the process, the pellet was found by mean of energy dispersive X-ray spectroscopy (EDS) to consist mainly of Bi-2223, with considerable amount of Bi-2201, the Bi-free 014x24-phase, Cu-free phase and silver particle. Fig. 11 shows the cross-section of the Bi-2223 pellet. It can be noticed that the degree of contact between silver particles and Bi-2223 grains appears to be high. Bi-2223 grains follow the orientation of the silver surface, orienting their c-axis orthogonal to the silver surface. This phenomenon is particularly evident around the triangular shaped silver particle (T in Fig.11) located in the upper-central portion of the micrograph (Fig. 11). In Fig. 12, a large silver particle (~10 μ m) is delimited by the planar surface of Bi-2223 grains. There is also noticeable intergrowth of Bi-2223 crystals into the silver particle. So far, this phenomenon has not been thoroughly studied and a detailed investigation of the

conditions leading to the intergrowth would be necessary to understand its mechanism of formation.

4. Discussion

The fact that Bi-2212 crystals have their c surface in contact with impurity phases, supports the assumption that the interfacial of BSCCO crystal is minimized when the c surface is in contact with an impurity phase (Eq.1). The same claim can be made from the microstructural observations of silver substrate and particles with respect to Bi-2212 or Bi-2223 crystals (Fig.10-12). Having in mind these results, we will discuss under a new prospective the process of BSCCO in the following sections.

4.1. Nucleation

Crystals which have nucleated on a flat silver foil (or on the free surface) have a high probability of being oriented parallel to the interface, because their activation energy barrier for nucleation is lower (see Sect.3.1.1). Consequently, in the absence of other concurring nucleation phenomena, the parallel alignment of crystals in contact with the substrate (or free surface) will propagate from the substrate (free surface) inward into the film, leading to a highly textured sample. However, secondary phases, such as the Bi-free phase, always present in the peritectic liquid, may be a good source for the nucleation of 2212 grains. Nevertheless, the surface of secondary phase particles is randomly oriented

with respect to the substrate, and consequently, 2212 crystals nucleating on secondary phases are not aligned with respect to the silver substrate. In summary, even when the mechanism of homogeneous nucleation is absent, heterogeneous nucleation cannot be responsible for the texture observed in Bi-2212 samples.

4.2. Crystal Growth

Consider now the evolution of superconductor crystals in the early stage of crystal growth during processing at high temperatures. A single Bi-2212 crystal in the peritectic liquid is subjected to a high thermal agitation (proportional to $k_B T$, where k_B is the Boltzmann constant and T is the absolute temperature). In addition, other phenomena, such as the difference in density between the 2212 crystals and the peritectic liquid, the presence of surface charges on the superconductor crystals and the convective motion of the liquid may enhance the mobility of a superconductor crystal. As a result, crystals growing in the peritectic liquid can be considered mobile. This argument is supported by two experimental observations. First, samples that were melt-processed under a high magnetic field exhibited rotation of superconducting crystals during early crystal growth [12]. Second, in situ observations with a high temperature optical microscope showed Bi-2212 crystals floating on the free surface [9].

Having this in mind, let us examine the case of a growing superconductor crystal in the process of coming into contact with another Bi-2212 crystal floating in the liquid. The more energetically favorable contact arising between Bi-2212 crystals is between planar

surfaces (Eq. 7-8). As a consequence Bi-2212 crystals will likely rotate their ab-planes parallel to each other (Fig. 13.a). Thus, we may predict that superconductor crystals will begin to form regions, or colonies, of aligned grains. As these colonies grow, they become less mobile, an effect of the augmented inertia and the concomitant decrease in the amount of available liquid. Ultimately, as the liquid disappears (Fig. 13.b) colonies will not be able to move and they will impinge upon each other without changing their orientation. Consequently, in the absence of planar constraints, the grains will be locally aligned, but will not exhibit long range order as a result of impingement between colonies with different orientations. This situation is typically observed in bulk specimens such as pellets [8], where Bi-2212 crystals are arranged in bundles of similarly oriented grains while the orientation of the bundles themselves appear to be random through the entire cross section.

Long range order may be attained when planar constraints are present, in the case of thick films or tapes. In these conditions, superconductor crystals will preferentially adhere to the silver substrate (or the free surface) with the planar surface, resulting in a c-axis orientation perpendicular to the silver substrate (or free surface) (Sect. 3.1.2). Moreover, grains aligned with the substrate may transfer their c-axis alignment to adjacent grains. In this way the orientation of the superconductor crystals may propagate across the oxide film. Evidently, the influence of the silver substrate or free surface on the texture of the grains will decrease with distance from the surface. In this manner, thicker films exhibit a lower degree of texture.

Besides the sample thickness, the rate of cooling affects the texture development in melt-processed thick films. Based on the above discussion, two misaligned crystals may align their c-axis if they come in contact and adhere through their planar surfaces. However, when the amount of liquid phase is small the rotation of superconductor crystals will be impeded by solid obstacles and consequently crystal alignment will be hindered. On this basis, it is reasonable to infer that when the rate of cooling is slow ($10^{\circ}\text{C}/\text{hour}$) the system will spend more time in a regime during which alignment of the crystals may take place and texture can be maximized. However, for a fast cooling rate ($1^{\circ}\text{C}/\text{min}$), little time is allowed for the superconductor crystals to align before impingement becomes dominant. Thus, a slow cooling rate during crystal growth will maximize the texture. Experiments performed with different cooling rate have shown that slow cooling rates near the solidus temperature result in thick films or tapes with the highest degree of texture [10].

The development of texture is also influenced by large secondary phase particles (or pores) during crystal growth. Since superconducting crystals can decrease their interfacial energy by having their planar surface in contact with a secondary phase particle (see Sect. 3.2), general alignment with the substrate is more unlikely to occur. As a consequence, the texture of the superconducting phase in the proximity of large secondary phase particles will be poor. Furthermore, since Bi-2212 thicker films present a larger amount of impurity phases [12], the misalignment effect due to the presence of impurities will be greater in these samples.

4.3. Alignment in Bi-2223

While the texture development in Bi-2212 films can be thoroughly addressed by Eq.1, further assumptions are required to fully understand the mechanisms of alignment of Bi-2223 platelets. In fact, the texture development of Bi-2223 tapes, besides the role played by phase transformations [13], is complicated by the pressing and rolling operations between the heat treatment sequences. As a consequence, the alignment process is strongly affected by various factors, such as the precursor powder and heat treatment process. Notwithstanding this, the alignment has been found to be partially or completely achieved before the transformation from Bi-2212 to Bi-2223 occurs [13]. Thus, the mechanisms of alignment for Bi-2212 grains described above continues to play a prominent role in the formation of Bi-2223.

4.4 The role of Silver

So far, metallic silver has been preferentially adopted for the preparation of Bi-2212 and Bi-2223 superconducting samples. Silver constitutes an appropriate substrate for Bi-based superconductors because it fulfills the following important requirements. These are (1) silver has a higher melting point than the superconductor, (2) inertness in contact with the superconductor material during the process and (3) high oxygen permeability. These properties, together with the fact that the presence of silver offers a high thermal conductivity, low resistivity and enhances the mechanical properties of the sample, have made silver the best substrate for Bi-based superconductors.

In addition, it has been also argued that silver could play a special role in enhancing the texture of Bi-2212 and Bi-2223 [14]. In particular, it has been proposed that an increase in texture is due to the fact that silver induces a decrease of the solidus temperature of Bi-2212 by up to 30K [14]. While silver has a beneficial influence on the Bi-2212 system, allowing the melt-process to be performed at lower temperatures with minor vaporization of Bi, the hypothesis that the texture is a consequence of the shift in the Bi-2212 solidus temperature is more arguable.

Based on the present work, we suggest that the effect of silver on the solidus temperature of Bi-2212, and its role in enhancing the development of the texture in Bi-2212/Ag films and tapes are two separate mechanisms. While the effect of silver on the solidus temperature is the result of the formation of an eutectic phase [15] between Bi-2212 and silver, its role in enhancing the texture development can be a consequence of Eq.1.

Finally, the fact that the texture development in BSCCO/Ag tapes could follow from interfacial effects suggests that other materials which satisfy Eq.1 and do not react with the BSCCO material could also constitute a suitable substrate. Gold could be a good candidate, because it has the same crystal structure and similar electronic configuration as silver. Experiments performed with this noble metal have proven that textured Bi-2212 films may be produced by a partial melt process on a gold substrate, although with different amounts of secondary phases [3, 16]. However, this difference is imputable to the diverse effect of gold on Bi-2212 phase stability. While gold does not affect the melting temperature of Bi-2212, silver does. In fact, when Bi-2212 has been processed on a substrate composed of an Ag-Au alloy, no relevant difference have been noticed in the

critical current density with respect to the pure silver substrate [17]. Based on this result, it is predictable that with the addition of silver powder, Bi-2212 could be processed on a gold substrate following the same heat treatment used for the silver substrate. The surface of gold will have the advantage of not degrading when BSCCO melts, whereas silver diffuses and roughens its surface.

5. Conclusions

Interfacial energy effects between BSCCO, silver (as a substrate or dispersed particle) and secondary phases have a crucial role in the texture development of BSCCO superconductors.

It has been shown that the interfacial energy of a BSCCO crystal is minimized when the planar surface of the crystal is in contact with a solid surface. This fact results in two important consequences. 1) Secondary phase particles have a deleterious effect on the texture formation. 2) The silver substrate enhances the texture formation of superconductor grains by offering a flat surface with a favorable interfacial energy for Bi-2212 grain alignment.

Acknowledgements

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Figures:

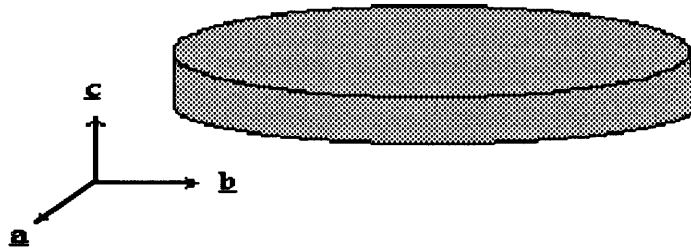


Figure 1. Schematic illustration of a Bi-2212 platelet grain. a, b, c are the crystallographic directions

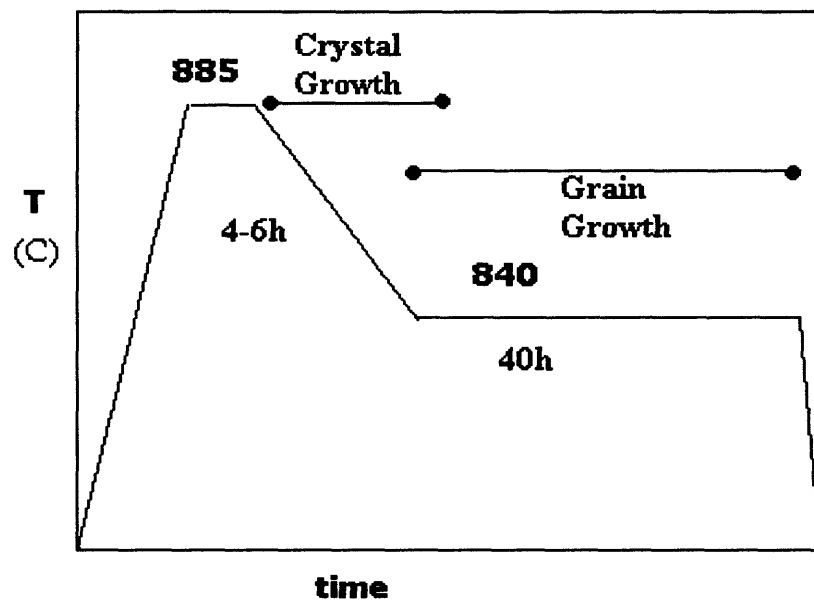


Figure 2: Heat treatment sequence for melt-processed Bi-2212/Ag thick films.

Heterogeneous Nucleation Model

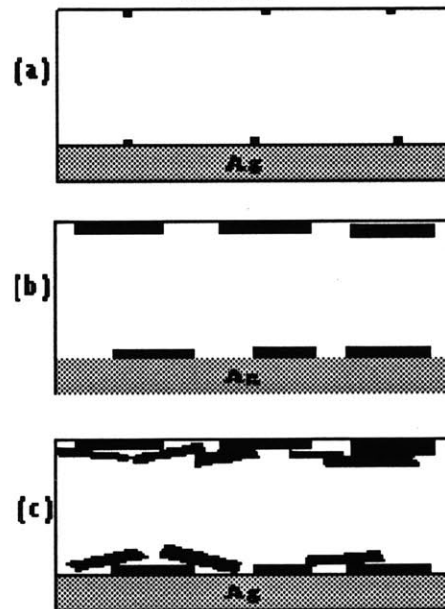


Figure 3: Model based on preferred heterogeneous nucleation [Kase]: (a) Nucleation starts at the Ag/oxide interface or at the free surface; (b) Grains grow initially aligned with the free surface or the substrate; (c) As the solidification proceeds inwards the alignment deteriorates, since the solid layer of Bi-2212 already formed is rougher than the silver substrate or free surface .

Buoyancy Model

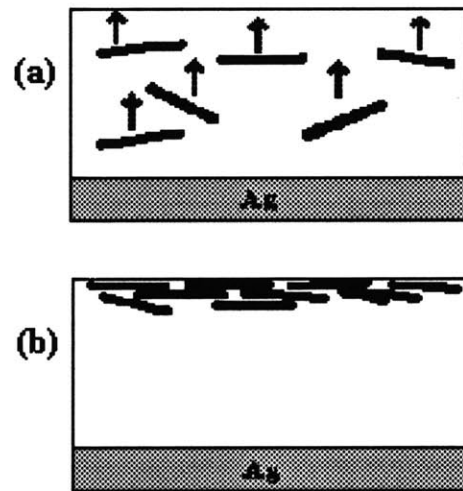


Figure 4: Model based on the different density between the peritectic liquid formed during partial melt and the Bi-2212 grains [Hell93]: (a) if 2212 grains are lighter than the surrounding liquid they be driven upward by Archimede's force and (b) subsequently sink at the top.

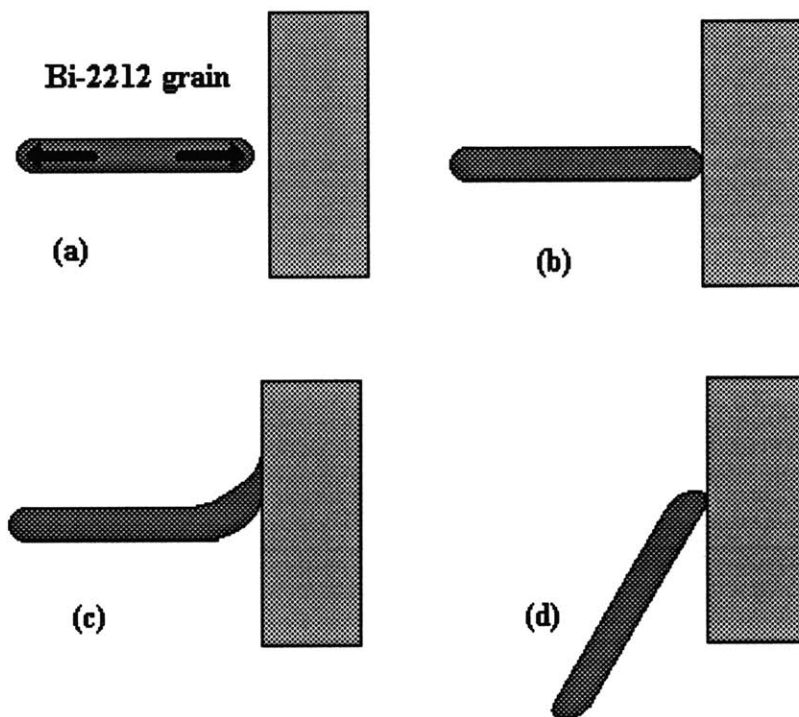


Figure 5. Schematic illustration of the alignment mechanism based on the anisotropic growth rate. (a) Crystal growth proceeds mainly along the ab -planes (same direction of the black arrows). If a small crystal encounters an obstacle (b), it is very unlikely that the growth along the ab -plane stops and therefore the grain may bend (c). The distortion of the atomic bonds imposes a force on the grain which results in partial alignment with the obstacle [lang].

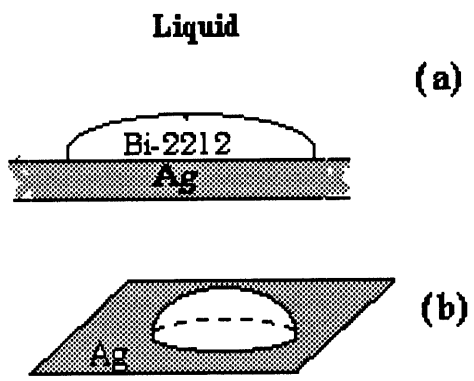


Figure 6. Schematic illustration of a spherical cap superconductor embryo nucleating on a silver surface: (a) cross section and (b) 3-d view.

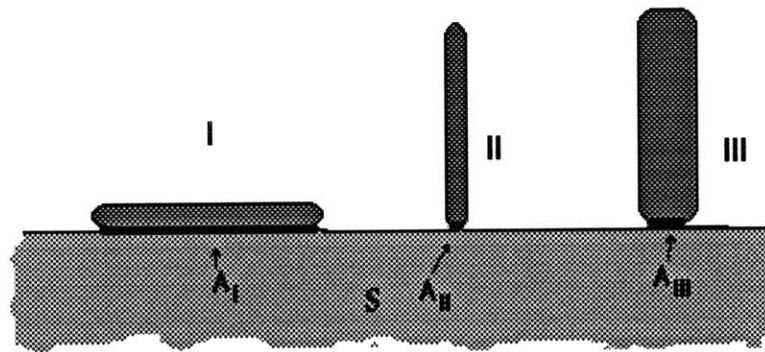


Figure 7. Bi-2212 platelet crystals in contact with a surface S. Crystal I is in contact with the \underline{c} surface, whereas crystals II and III are in contact with a surface different from the \underline{c} surface. A_I , A_{II} and A_{III} are the surface of contacts of grain I, II and III respectively.

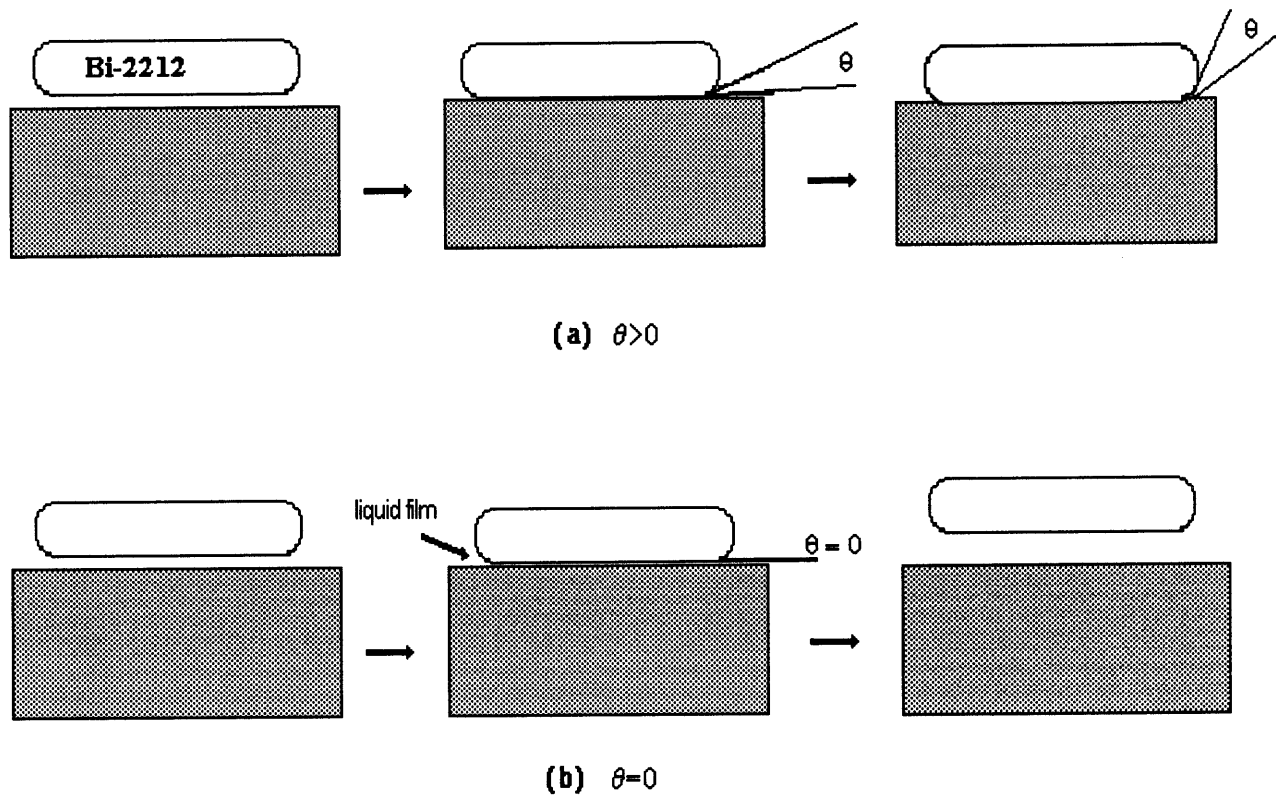


Figure 8. Schematic representation of two different cases for a Bi-2212 grain in virtual contact with a foreign surface and having a dihedral angle θ . Case (a), for $\theta > 0$ the contact is stable. Case (b) for $\theta = 0$ a thin film of peritectic liquid wets the surface and impedes the contact. Eventually the grain moves away.

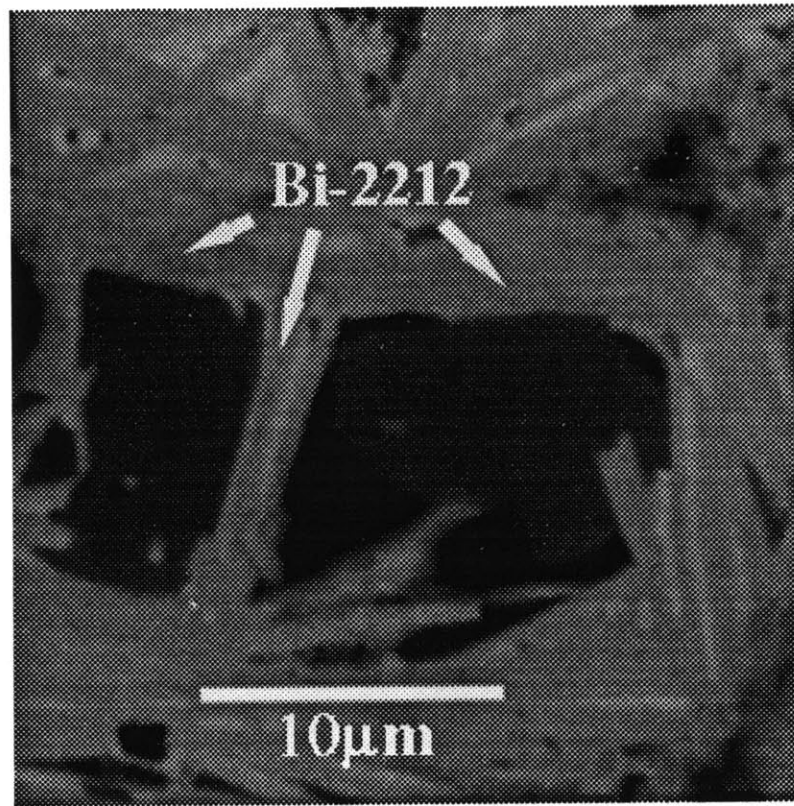


Figure 9. SEM backscattered electron images of the cross-section of a Bi-2212 pellet. EDS analysis revealed the black particles to be Bi-free impurity phases, the dark gray Bi-2212, the light gray as Bi-2201.

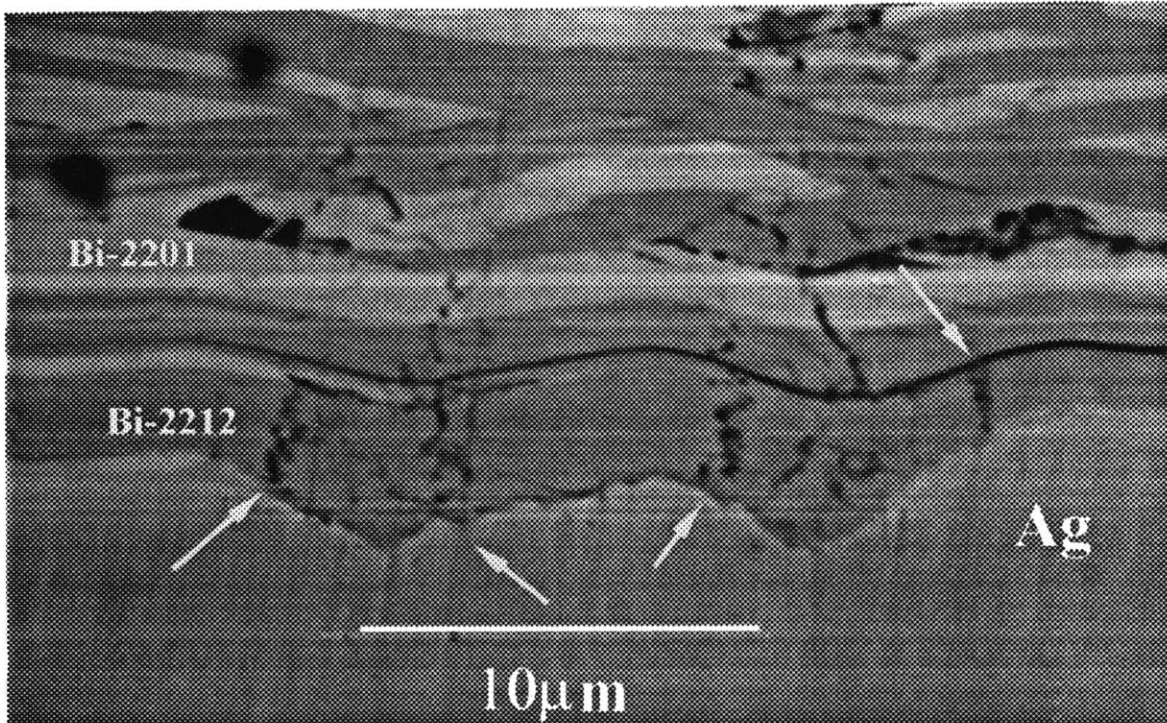


Figure 10. SEM Backscattered electron image. Cross-section of a melt-processed Bi-2212/Ag thick film. Dark gray grains have been identified, by EDS, as Bi-2212 and light gray grains as Bi-2201. The white arrows indicate cracks in the superconductor layer.

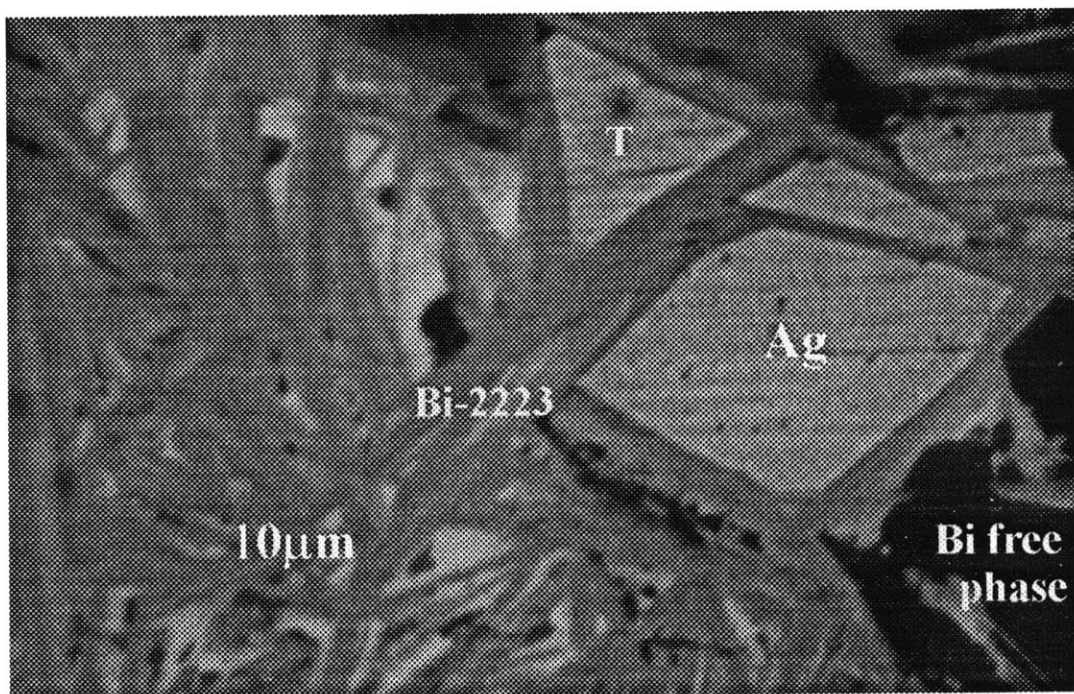


Figure 11. SEM back-scattered electron images of the cross-section of a Bi-2223+ 5wt% Ag pellet. The black particles have been identified, by EDS, as Bi-free impurity phases, the dark gray as Bi-2223 and the light gray particles on the upper right corner of the micrograph as silver. On the central-upper part of the micrograph a white "T" indicates a silver particle of triangular shape.

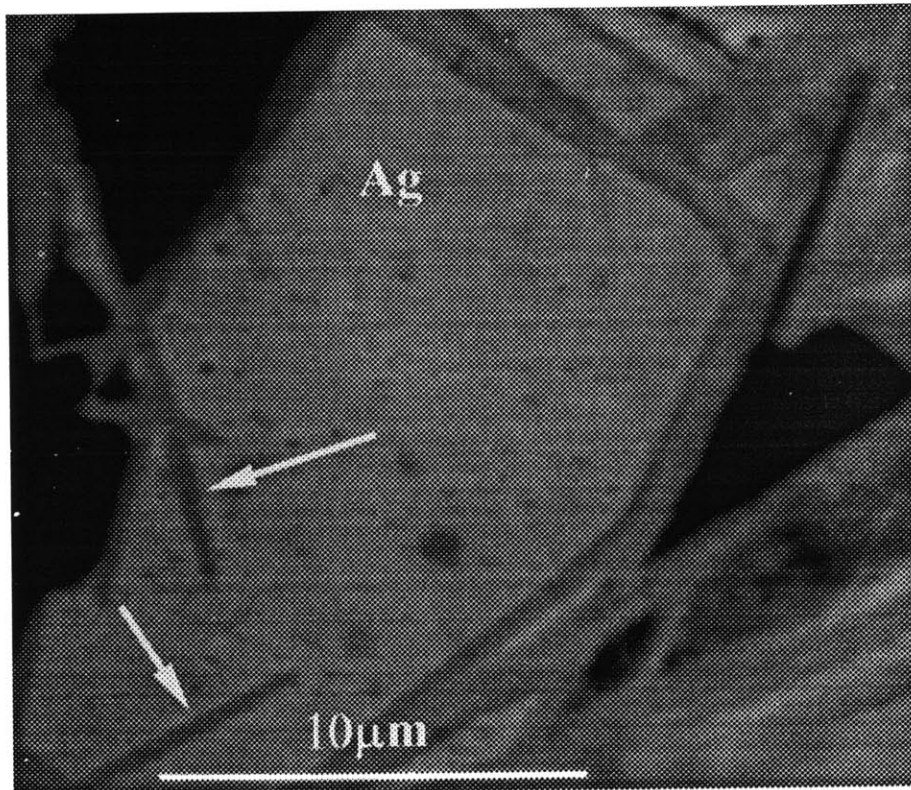


Figure 12. SEM backscattered electron image of the cross-section of a Bi-2223 + 5wt% Ag pellet. The black particles have been identified, by EDS, as Bi-free impurity phases, the dark gray as Bi-2223 and the big light gray particle as silver. White arrows indicate regions of intergrowth of Bi-2223 crystals in the silver particle.

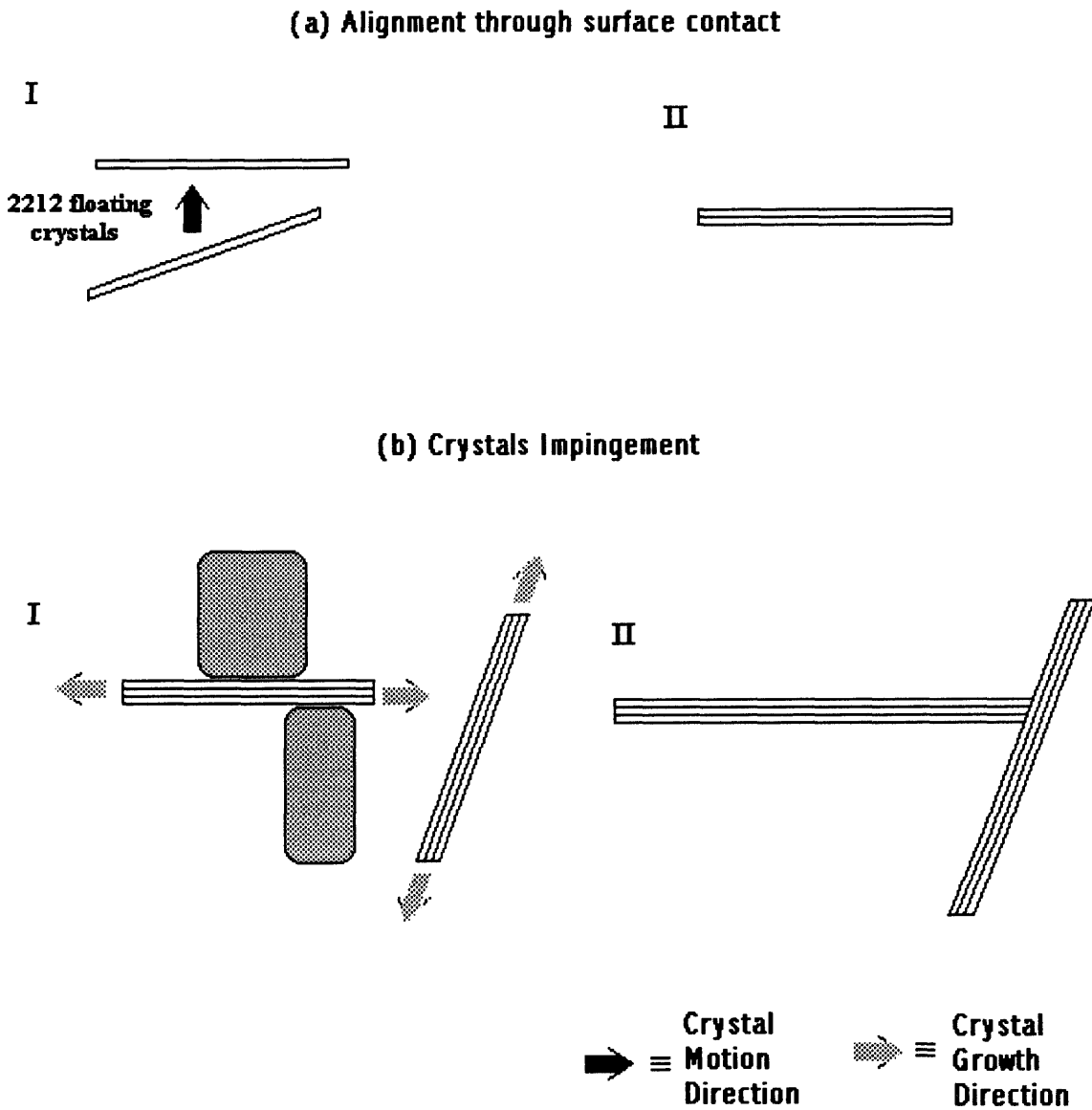


Figure 13. Schematic illustration of two modes of interaction between Bi-2212 crystals, during the crystal-growth regime. Mode (a): two Bi-2212 crystals in contact with each other (I) may rotate and minimize their surface tension by stacking the c axis parallel to each other (II). Mode (b): If the rotation of Bi-2212 crystals (or colonies) is hindered by solid obstacles (I), crystal growth may result in impingement of colonies with high angle misalignment (II)

CHAPTER 2.

The Influence of Elevated Magnetic Fields on the Texture Formation of Melt-Processed Bi-2212

Abstract: Melt-processing of BSCCO high- T_C superconductors 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. This result may have important consequences on the large-scale implementation of this process.

1. Introduction

The use of High- T_c superconductor oxides (HTS) for conductor applications requires the presence of a preferred orientation of the superconductor grains, in order to minimize the grain boundary weak links, resulting in a increased transport critical current density (J_c) [1]. One way of aligning HTS grains is to utilize a high magnetic field. If a grain exhibits an anisotropic paramagnetic susceptibility in its normal state, then when placed in a magnetic field, the magnetic energy is minimized when the superconductor grain aligns 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 the texture development could be combined with other techniques. Recently, Tournier et al. [2] have employed a high magnetic field together with the hot pressing technique to enhance texture in Bi-2223 samples.

Despite some encouraging results [3,4], the prospect of using high magnetic fields during extended portions of the superconductor fabrication is unattractive for large-scale implementation. 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 manner in which the grain-alignment is achieved. Induced grain alignment has been reported both during the solidification from the molten state [5] or during the annealing process [6,7], suggesting that the alignment may occur in two ways: 1) Rotation of paramagnetic superconductor crystal induced by a magnetic field when a liquid phase is present in the system. 2) Selective grain growth allowing grains aligned with the magnetic field to grow at the expense of misaligned grains during the grain growth regime [8].

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In a recent paper [9], Ferreira et al. proposed a theoretical 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. At later stages of growth, grain-to-grain interaction hinders the magnetic field induced alignment. If the results of this model are valid, a short time exposure to the magnetic field could be sufficient to enhance the texture of HTS's. Consequently, the opportunity of employing magnetic fields for processing HTS's could be reconsidered for large-scale industrial applications.

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

2. Experimental Procedure

Samples preparation

Bi-2212/Ag thick films were prepared with highly pure (99%) Bi_2O_3 , SrCO_3 , CaCO_3 and CuO weighed according to the nominal composition $\text{Bi}_{2.15}\text{Sr}_{2.05}\text{Ca}_{0.95}\text{Cu}_2\text{O}_x$. The mixed powders were calcinated at 780°C , 800°C and 820°C in air for 12, 12 and 70 hours 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 minutes and the resulting homogeneous black liquid poured on silver ribbons of rectangular shape (2mmx12mm). Following the evaporation of ethanol at room temperature, the samples were melt-processed in a vertical furnace placed inside a toroidal magnet. The final thickness of the processed films was $30 \pm 5\mu\text{m}$.

The heat treatment chosen was designed to verify the possibility of enhancing the texture formation with short time application of a magnetic field and to test the relevance of crystal rotation versus selective grain growth to align 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 $1^\circ\text{C}/\text{min}$, a second stage of cooling to 840°C at a rate of $0.1^\circ\text{C}/\text{min}$ and an isothermal annealing at 840°C for 40 h (Fig.1). A temperature of 860°C was chosen because it is below the solidus temperature [10] and consequently crystal

rotation is inhibited. In this fashion, we may determine whether the presence of a magnetic field 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). In this fashion, 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 with the application of the magnetic field during both stages of cooling (880-840C). Films labeled B were melt-processed with the application of a magnetic field during the first stage of cooling (880-860C), so that the magnetic field could play a primary role during nucleation and crystal growth. Films labeled C were melt-processed with the application of the magnetic field during slow cooling (860-840). In this manner, the influence of the magnetic field is expected to be limited to the grain growth regime. 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 different stages of the melt-processing of these samples.

Tab1. The use of magnetic field (7T) in the melt-process of Bi-2212 films.

SAMPLE	880-860 (20min)	860-840 (200min)	840 (40h)
	Crystal Rotation	Selective Grain Growth	
	Magnetic Field	Magnetic Field	Magnetic Field
A	ON	ON	OFF
B	ON	OFF	OFF
C	OFF	ON	OFF
D	OFF	OFF	OFF

Sample characterization

Surface X-ray diffraction 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 X-ray diffraction spectra by using the Lotgering factor (F) [11], which can be calculated as follows:

$$F = (P - P_0) / (1 - P_0) \quad (1)$$

where $P = \sum_1 I_{00l} / \sum_{(hkl)} I_{hkl}$ 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 (unoriented) to 1 (completely oriented). The X-ray diffraction work was performed in a Rigaku 300 X-Ray diffractometer, using CuK α X-ray radiation at 60 KV and 300mA.

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 4-probe DC method. A criterion of $1\mu\text{V}/\text{cm}$ was used to determine J_c .

3. Results and Discussion

Surface X-ray diffraction patterns of film A (Fig.2), B (Fig.3), C (Fig.4) and D (Fig.5) show strong (00l) peaks, very weak (2210), (2214) peaks and a few 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 X-ray diffraction pattern are characteristic of films exhibiting a strong c-axis grain alignment orthogonal to the film surface.

In order to differentiate the degree of texture among films A, B, C and D, the Logering factor (F) was calculated, as shown in Fig.6. 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 A, in which both crystal rotation and selective grain growth may have occurred (see Table 1). The application of a magnetic field during the first stage of cooling (films B), where crystal rotation may

occur, seems to be more effective in enhancing the texture than the application of a field during grain growth (film C).

SEM backscattered images of polished cross-sections of films A, B, C and D are shown in Fig.7, 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). 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.8, the transport critical current densities of the films, measured at liquid helium temperature, are plotted as a function of the process type. The maximum value in J_c occurs in films where the magnetic field was present during the whole cooling process (film A). The application of a magnetic field during the solidification from the molten state (films B) results in higher J_c 's than films C, where the magnetic field is present during grain growth. The process in the absence of a magnetic field (films D) exhibits the lowest J_c , however its J_c value is very close (within the standard deviation) to the critical current density obtained for films C. The improvement in J_c for the 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.6. The difference in texture improvement is difficult to distinguish from the SEM micrographs (Fig.7), 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 minutes, a J_c enhancement of approximately 50% was achieved in comparison with samples processed in the absence of magnetic field. On the other hand, the application of a 7 T magnetic field during the grain growth process improved the critical current density by less than 10%.

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 densities of films A and B, whose only processing difference was the absence of a magnetic field during grain growth in film B, corroborates the hypothesis that texture formation can only be weakly enhanced during grain growth. This result could have been expected, since several experimental works reported a J_c improvement in samples sintered for long times (>10 hours) under a high magnetic field, i.e. in the grain growth regime [6,7]. This conclusion is in agreement with the analysis developed by Ferreira et al. [9]. 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 exposure are required for the magnetic field to be effective in enhancing texture during grain growth.

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 nucleation energy for nuclei aligned with the magnetic field. However, it has been shown [9] that the effect of elevated magnetic field on the nucleation rate is irrelevant. On the other hand, crystal rotation may occur because a superconductor crystal immersed in a liquid, under a magnetic field, experiences a torque:

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

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 θ is the angle between the magnetic field and the c -axis of the crystal. The torque tends to cause an angular rotation 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 τ 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 τ , 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 1C/min) because when the cooling is faster, the amount of secondary phase, detrimental for J_c , increases drastically [12]. 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. Conclusion

The degree of texture and transport critical current density in Bi-2212 thick films can be enhanced by a short time application (20minutes) of a magnetic field during the early stages of solidification. The mechanism behind this effect resides in 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.

Acknowledgment

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Figures

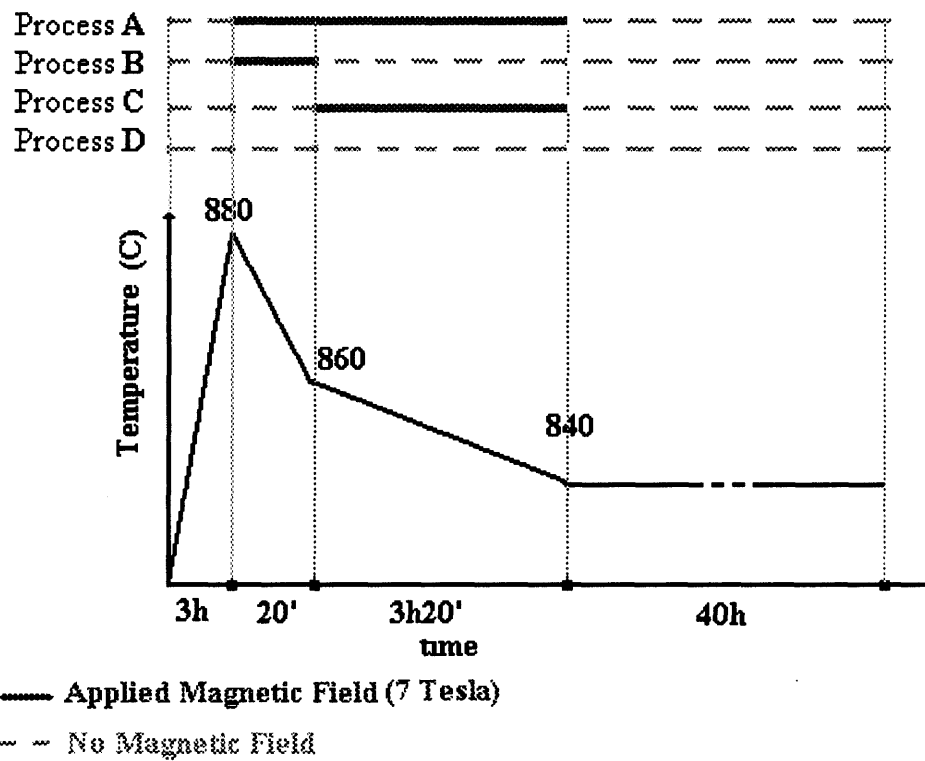


Figure 1. The use of a 7T magnetic field in the melt-process of Bi-2212/Ag thick film A, B, C and D.

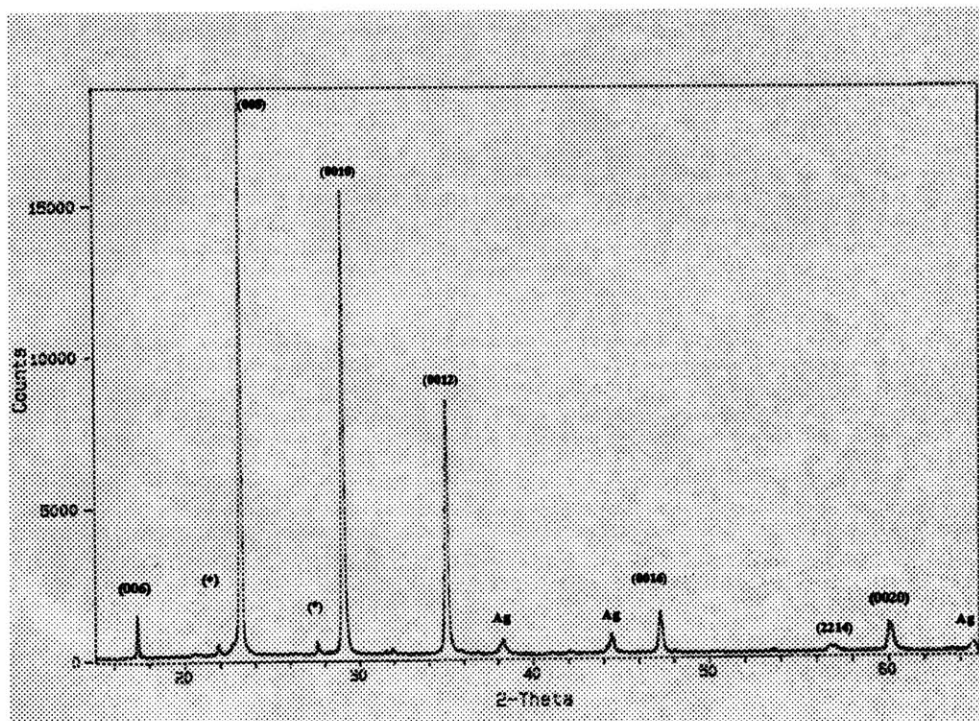


Figure 2. Surface X-ray diffraction of film A. The presence of impurity phase peaks is indicated with symbol (*).

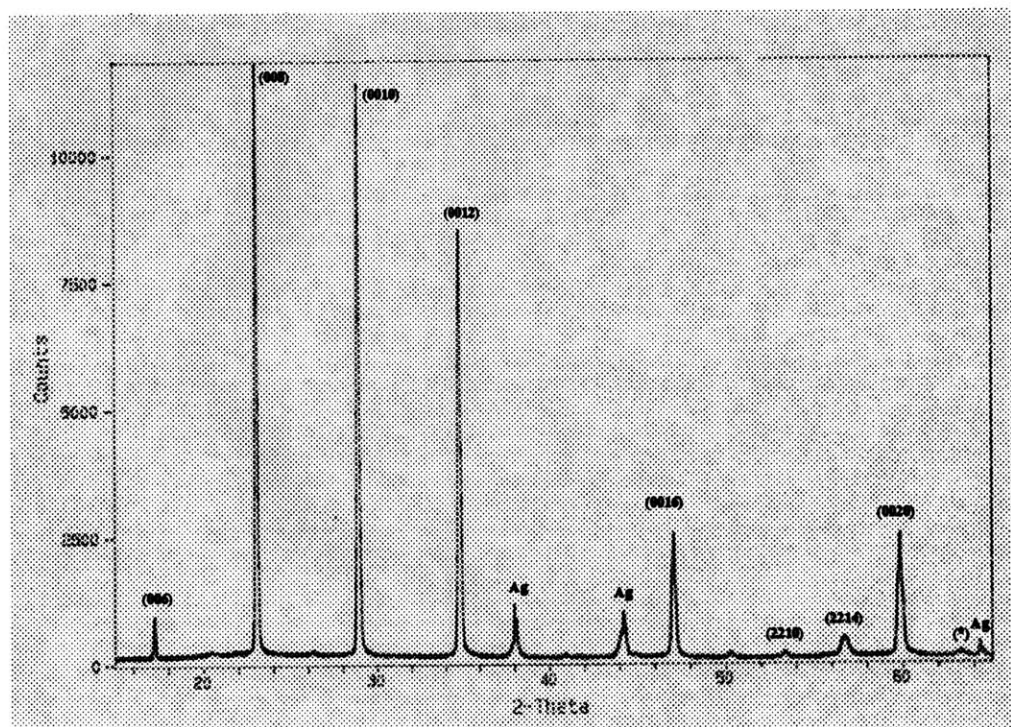


Figure 3. Surface X-ray diffraction of film A. The presence of impurity phase peaks is indicated with the symbol (*).

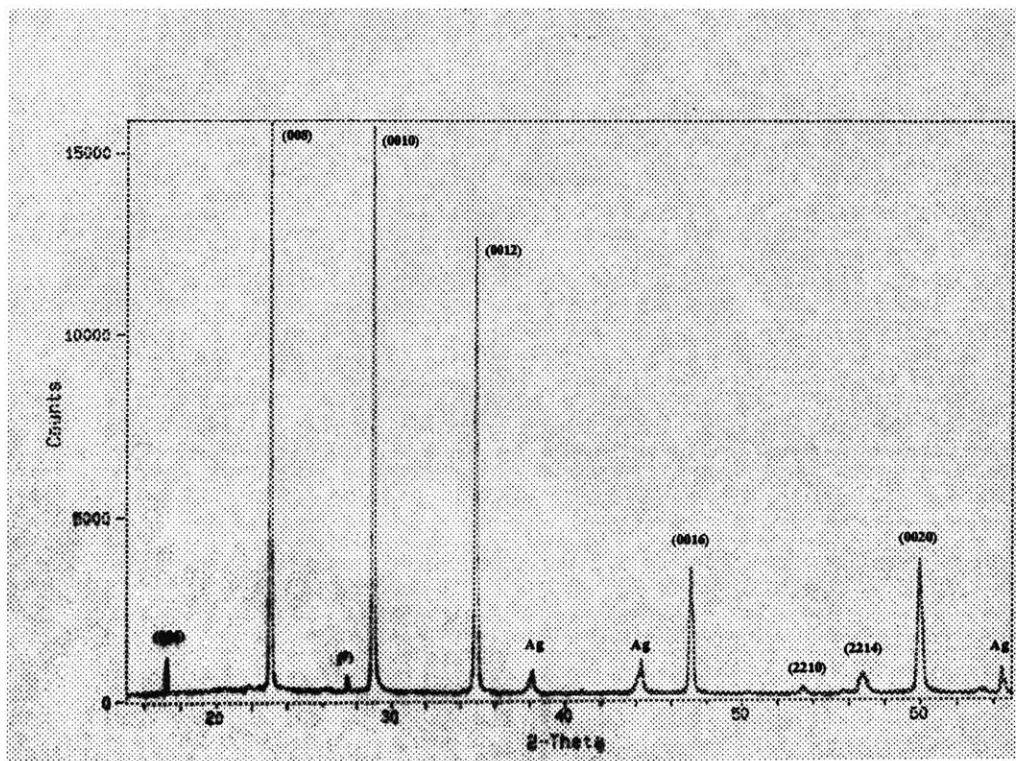


Figure 4. Surface X-ray diffraction of film C. The presence of impurity phase peaks is indicated with the symbol (*).

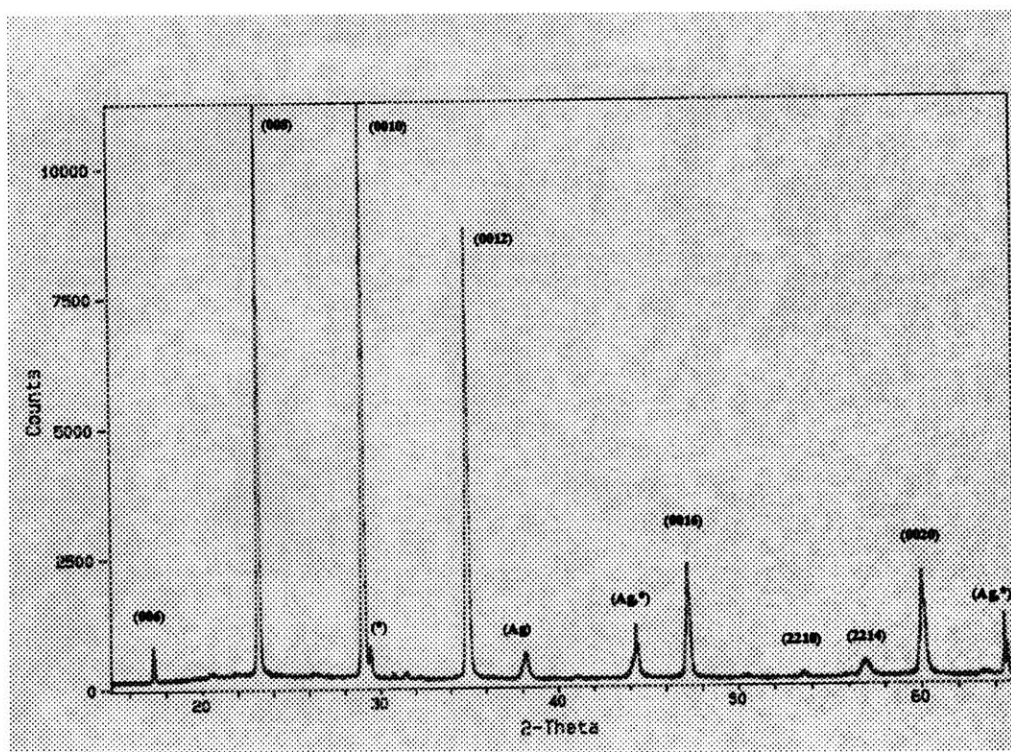


Figure 5. Surface X-ray diffraction of film D. The presence of impurity phase peaks is indicated with the symbol (*).

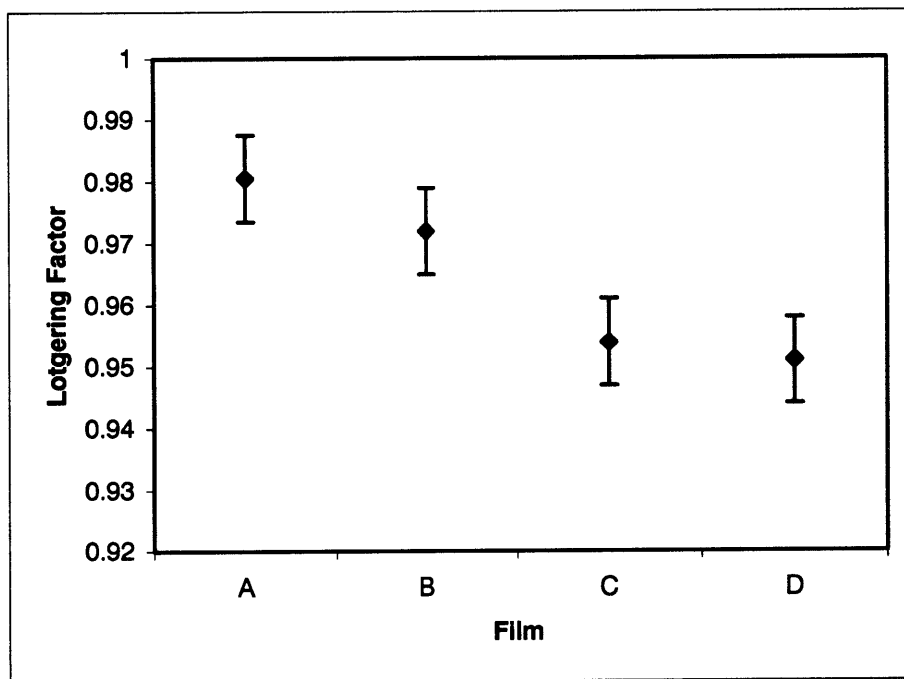


Figure 6. Average Lotgering factors of film A, B, C and D, calculated on the basis of three samples

a)

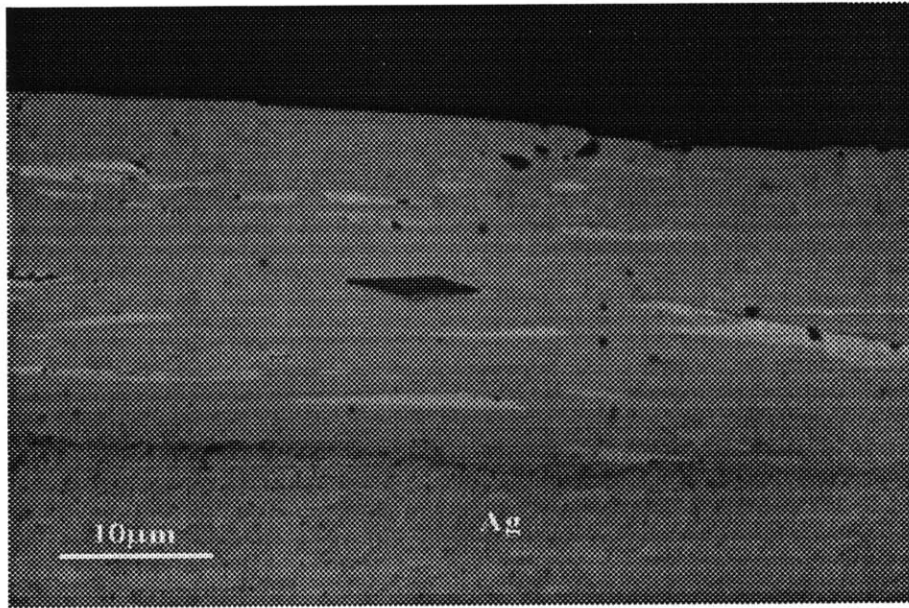


Figure 7. a) Backscattered electron image of Bi-2212/Ag cross section melt-processed under a 7T magnetic field during both cooling stages (880-840C, Film A) .

b)

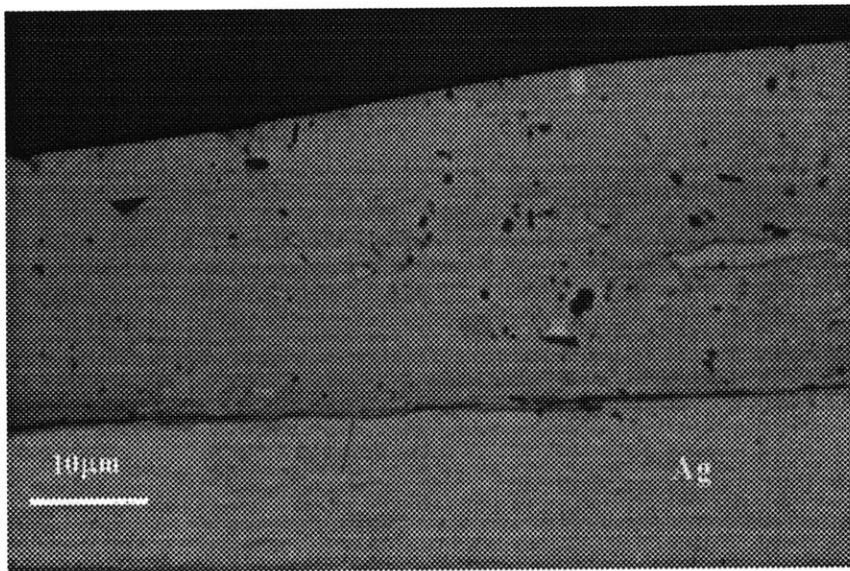


Figure 7.b). Backscattered electron image of Bi-2212/Ag cross section melt-processed under a 7T magnetic field during the first stage of cooling (880-860C, Film B);

c)

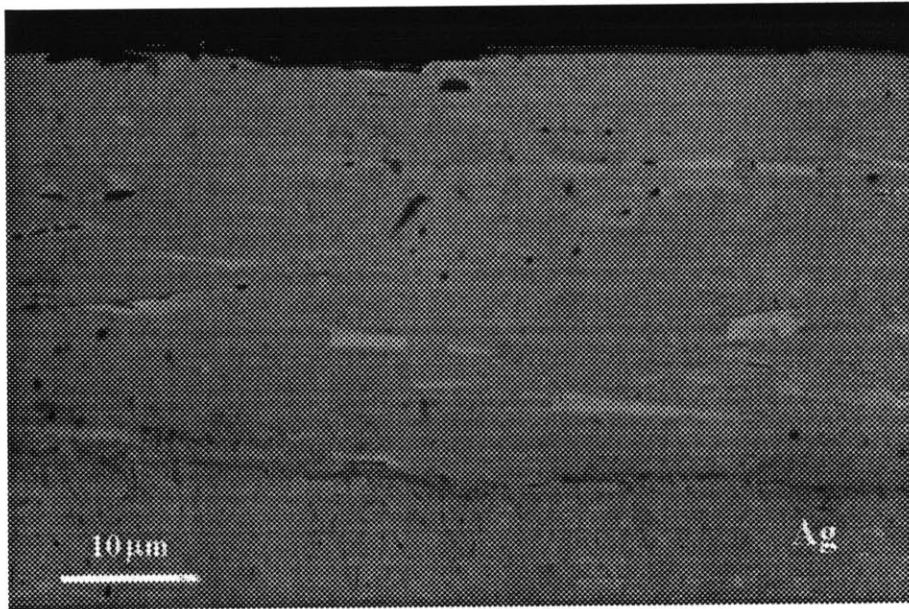


Figure 7.c). Backscattered electron image of Bi-2212/Ag cross section melt-processed under a 7T magnetic field during the second stage of cooling (860-840C, Film C).

d)

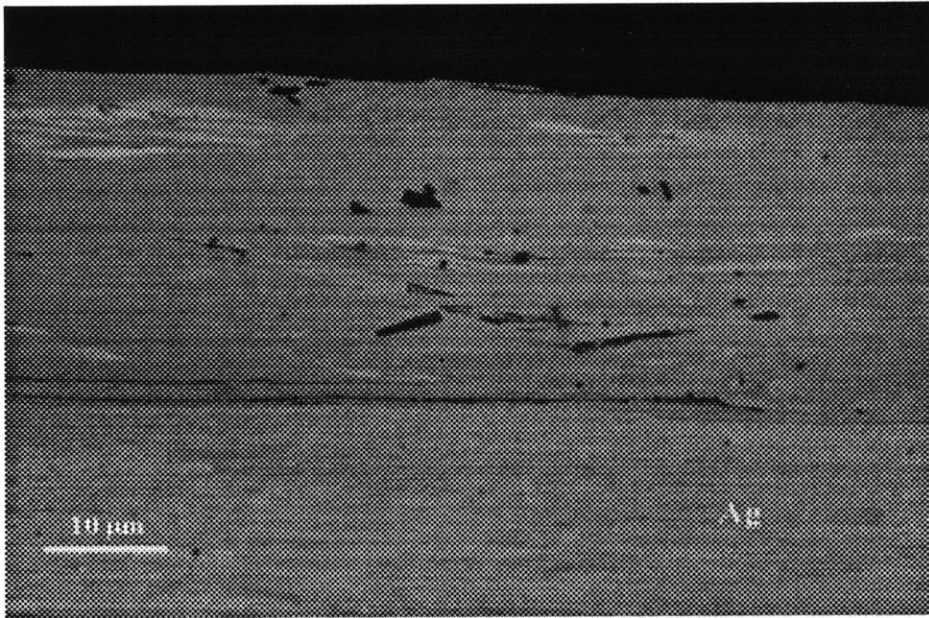


Figure 7.d). Backscattered electron image of Bi-2212/Ag cross section melt-processed in absence of magnetic fields (Film D).

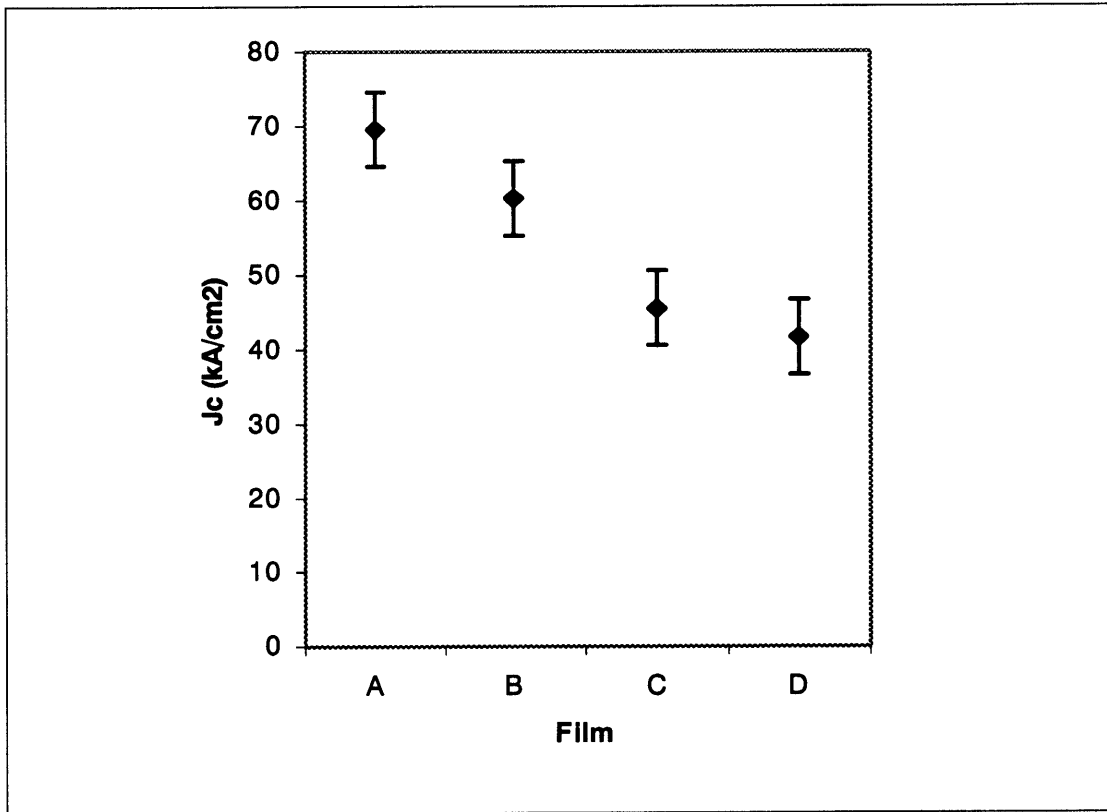


Figure 8. Average Critical Current Density of film A, B, C and D, calculated on the basis of three samples. Measurements were performed in liquid Helium with the 4-probe DC method. A criterion of $1\mu\text{V}/\text{cm}$ was used to determine J_c .

Conclusion

A thorough study of the mechanisms leading to a textured BSCCO superconductor has been undertaken. In particular we have focused on the Bi-2212/Ag system because this system offers the advantage of a simpler and more reliable processing technique, compared to the Bi-2223 system where the final microstructure is strongly influenced by precursor powders, oxygen pressure and small variations in the heating sequence.

In the absence of a high magnetic field, texture formation is controlled principally by interfacial energy effects. In particular, it has been noticed that Bi-2212 platelet grains tend to align with their c axis orthogonal to the silver (substrate or dispersed particle) or impurity phase surface. This mechanism implies that the presence of a silver substrate may enhance the alignment of the superconductor grains close to the Bi-2212/Ag interface whereas impurity phases and dispersed silver particles have a disruptive influence on texture formation. Consequently, due to the fact that thicker superconductor films ($>40\mu\text{m}$) exhibit a larger amount of secondary phases, the degree of texture in these films will be modest. One possible route to reduce the disruptive effects of impurity phase particles on texture formation is to control the shape of the impurity particles. In fact, for particles elongated in one or two directions (needle- or plate-like), the alignment of Bi-2212 grains around them could be in the same direction of the overall alignment in the sample. Thus the effect of these particles would result in a texture enhancement. Confirmation of the validity of this technique can be found in the texture enhancement observed in bulk Bi-2212 with dispersed MgO whiskers [1].

One possible technique to overcome this disruptive effect in thicker samples is the use of a high magnetic field during the melt-processing. The grain alignment under the magnetic field occurs mainly during the early stages of solidification, when the superconductor crystals may easily be rotated by the magnetic field. In this case, even a short time application of the magnetic field can be effective for enhancing the texture of the film, making this technique more attractive for large scale applications.

Reference

[1] Y. Yan, M.A. Kirk and J.E. Evetts, *J. Mat.Res.*, 12,. 3009-3028, (1997).