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Texture in Melt-Processed Bi-2212

TH. LANG, D. BUHL, D. SCHNEIDER, S. AL-WAKEEL & L.J. GAUCKLER[1]

ETH Zurich, Department of Materials, Chair of Nonmetallic Materials, Swiss Federal Institute of Technology, CH 8092 Zurich, Switzerland

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Abstract. The high temperature superconducting phase $Bi_{2.2}Sr_{2.05}5Ca_{0.95}Cu_2O_x$ (Bi-2212) decomposes peritectically when heated above its solidus temperature and reforms during slow cooling from the partially molten state. In thick films of 60 μm the Bi-2212 grains grow directly from the melt when cooled at a rate of 5 K/h in oxygen atmosphere. The orientation of the nuclei in the melt is random. After nucleation the grains grow anisotropically, leading to a mica- or platelet-like morphology. Upon growth the Bi-2212 platelets encounter several obstacles, i.e. the sample boundaries, second phase grains and other platelets. Various reactions occur when their growth is hindered. They stop growing, change the direction of growth or even grow through the obstacle. A mechanism is proposed which allows small grains to turn themselves into a favorable orientation at their initial stage of growth. At the end of the partial melting process, these mechanisms lead to a textured microstructure in thick films.

Keywords: $Bi_2Sr_25CaCu_2O_x$, high temperature superconductor, partial melt processing, thick films, texture, grain alignment

1. Introduction

$Bi_2Sr_2CaCu_2O_x$, (Bi-2212 or *two-layer compound*) is an important compound for industrial applications because devices with high current carrying capacities even at 77 K have successfully been manufactured [1–4]. The highly anisotropic behavior of the two-layer compound requires well textured microstructures in order to get high critical current densities. Such structures can be obtained by the partial melting process of thick films [5], where high j_c values exceeding $3 \cdot 10^4$ A/cm^2 (77 K, 0 T, d $\approx$ 10 μm) were reported [6]. However, by increasing the sample thickness these values are significantly reduced to a few thousand A/cm^2 for thicknesses exceeding 500 μm [7–9]. This drop of j_c is mainly attributed to the loss of grain alignment with increasing sample thickness. It is worthwhile to note, that the absolute current carrying capacity of bulk samples is still higher than in thick films because the increase of j_c does not compensate the loss of cross section area when the sample thickness is reduced [10]. Therefore, it is of major importance to increase the cross section area without reducing j_c. This goal can only be reached when the mechanisms that lead to the well-textured microstructure in Bi-2212 thick films are understood.

Kase et al. [11] observed three important factors for grain alignment in melt-processed Bi-2212 thick films: Slow cooling from the maximum processing temperature to 860°C, the thickness of the oxide layer and the existence of a silver sheath. By comparing samples with varying thicknesses from 20 μm to 200 μm, they suggested that texturing proceeded from the sample surface and possibly from the oxide/silver interface inward.

Hasegawa et al. [12] prepared 10 to 15 μm thick Bi-2212 films by partial melting and observed that the Bi-2212 phase initially grew along the liquid surface. This growth was recognized to be very important to produce good c-axis alignment of the oxide layer.

Using in-situ high-temperature microscopy, Hasebe et al. [13] observed, that Bi-2212 platelets floated on the surface of partially molten thick films

during cooling from the maximum processing temperature. They assumed that texture of the Bi-2212 phase was strongly dependent on the free surface of the sample.

Aksenova et al. [14] prepared Bi-2212 tapes by powder-in-tube and subsequent partial melt-processing. They observed a correlation between the degree of grain alignment and the critical current density. For the texture formation of the Bi-2212 grains in the Ag sheath they proposed a new model which involves random nucleation of the Bi-2212 grains in the melt and highly anisotropic growth of the grains in a quasi two-dimensional environment. The possibility of any recrystallization process was strictly denied. Using computer calculations it was possible to compare this model with XRD pole figure measurements.

The influence of several sample and processing parameters (e.g. maximum processing temperature, film thickness, free surface, substrate material) on the alignment of the microstructure of Bi-2212 thick films [15] and tapes [16] has been investigated by Zhang and Hellstrom. It was observed that the aligned microstructure in fully processed samples is not formed initially when Bi-2212 begins to nucleate and grow, but forms in a latter stage of growth. The authors speculated that Bi-2212 nucleates and grows at random orientation in the initial stage of growth. During cooling grains oriented parallel to the substrate can grow to much larger size than grains with their a-b-planes (almost) parallel to the tape normal. In addition, it was observed that the overall grain alignment became better during annealing at 840°C. No exact mechanism for this behavior was suggested but it was assumed that favorably oriented grains consumed some of the smaller, misoriented grains and that favorably oriented grains rotated smaller, misoriented grains into favorable alignment. In case of the thick films an additional alignment mechanism occurring at the free surface due to surface energy effects was proposed because in Bi-2212 thick films a better grain alignment at the free surface than in the sample interior was observed.

Ray and Hellstrom [17] investigated Bi-2212 tapes produced by powder-in-tube and partial melt-processing. They proposed a model for the texture formation called ''opportunistic grain growth'' which is very similar to the mechanism suggested by Aksenova et al. [14]. Preferential alignment occurs when the shape of the local environment and the morphology of the grains favors grain growth in certain directions. However, no absorption of grains by growing grains is allowed.

In contrast to all reports mentioned above, Tenbrink et al. [18] have observed no texture in melt-processed Bi-2212 round wires with a core thickness of 600 μm to 700 μm.

The degree of grain alignment in a sample can basically be characterized by various methods. X-ray diffraction is a well-established technique which averages over the whole investigated sample area [19]. However, it does not allow any statement about the local arrangement of individual grains. Since the penetration depth of X-rays in Bi-Sr-Ca-Cu-Oxides is low (i.e. <10 μm) informations are limited to the surface area. Furthermore, the time needed to record a full XRD-pattern can be too long when rapid reactions occur [12]. A different method consists of quenching samples during the heat treatment in order to freeze the high temperature microstructure [12,15]. Cross sections of quenched samples can be analyzed optically and informations about nucleation, grain morphology, and local grain arrangements can be obtained. Even if mechanisms for the formation of aligned microstructures in melt-processed Bi-2212 thick films and tapes have been proposed, no satisfying model which can explain all the observed microstructural features was found.

We investigated the formation of the microstructure in partial melt-processed Bi-2212 thick films using a quenching technique and compared the microstructure of thick films with bulk samples. Special emphases was laid on the microstructural mechanisms occurring during solidification of the Bi-2212 thick films and bulk components.

2. Experimental

2.1. Sample Preparation

Powder with the stoichiometry $Bi_{2.2}Sr_{2.05}Ca_{0.95}Cu_2O_x$ was prepared by a standard calcination process [20]. This composition was chosen because it lies in the single phase region of the Bi-2212 phase at temperatures >800°C [21,22]. An organic, non-toxic slurry was prepared by mixing 100 g of the Bi-2212 powder, 1.5 g triolein, 18 ml ethanol, 5.0 g polyethylene glycol, and 4.5 g bis(2-ethylhexyl) phtalate in a planetary mill for 3 h. Then, 5.0 g poly(vinyl butyral) which was dissolved in 18 ml

Ethanol were added and the slurry was milled for one more hour. After degassing the slurry was cast onto glass and dried. Samples with a diameter of 11 mm were cut from the dried tape and the organics were burnt out at 550°C. For the heat treatments the green tapes were put on a silver substrate (d_{Ag}=100 μm). Bulk samples were prepared by pressing the raw Bi-2212 powder directly into a silver cup with a diameter of 12 mm at 170 MPa. The heat treatment for the thick films consisted of a partial melting step at 893°C, slow cooling to 850°C at a rate of 5 K/h, and isothermal annealing at 850°C for 48 h. Bulk samples were melted at 902°C and cooled at a rate of 5 K/h. In order to freeze the high temperature microstructure, the samples were fixed on a sample holder, suspended in a vertical furnace, and quenched in oil from various temperatures during the heat treatment. The heat treatment schedules are shown in Figs. 1a and 1b.

All heat treatments were done in an atmosphere of flowing oxygen (pO_2=1 atm), the final thickness of a processed tape was 60 μm, the thickness of the bulk samples was 1 mm.

2.2. *Sample Characterization*

The quenched samples were cut in two halves. One half was mounted in acrylic resin, ground and polished through 1 μm diamond using oil for all grinding and polishing steps. The cross section was analyzed by means of light microscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS).

In order to quantify the degree of alignment of the Bi-2212 grains, angles α_i ($i = 1, \ldots, n$) between the a-b-planes of the grains and an array of lines perpendicular to the substrate were measured in several cross sectional areas at the intersections of the array with the grains as outlined in Fig. 2. The array was chosen perpendicular to the substrate because most Bi-2212 platelets are oriented parallel to the substrate and therefore the probability of intersections was highest. For reasons of simplicity, angle α_i, which is the one smaller than 90° was measured. In order to get a small value for a grain almost parallel to the substrate, each angle α_i was subtracted from 90°, resulting in angles β_i, which correspond to the angles between the platelet planes and the substrate. These β_i angles were used for further interpretation. Grains with their a-b-plane parallel to the substrate show an angle β_i close to zero degrees, misaligned grains result in angles up to 90°. The orientation of the array of lines is not random relative to the sample but perpendicular to the substrate. Therefore, a Bi-2212 platelet oriented parallel to the substrate is more likely to be cut by the array than a grain oriented (almost) perpendicular

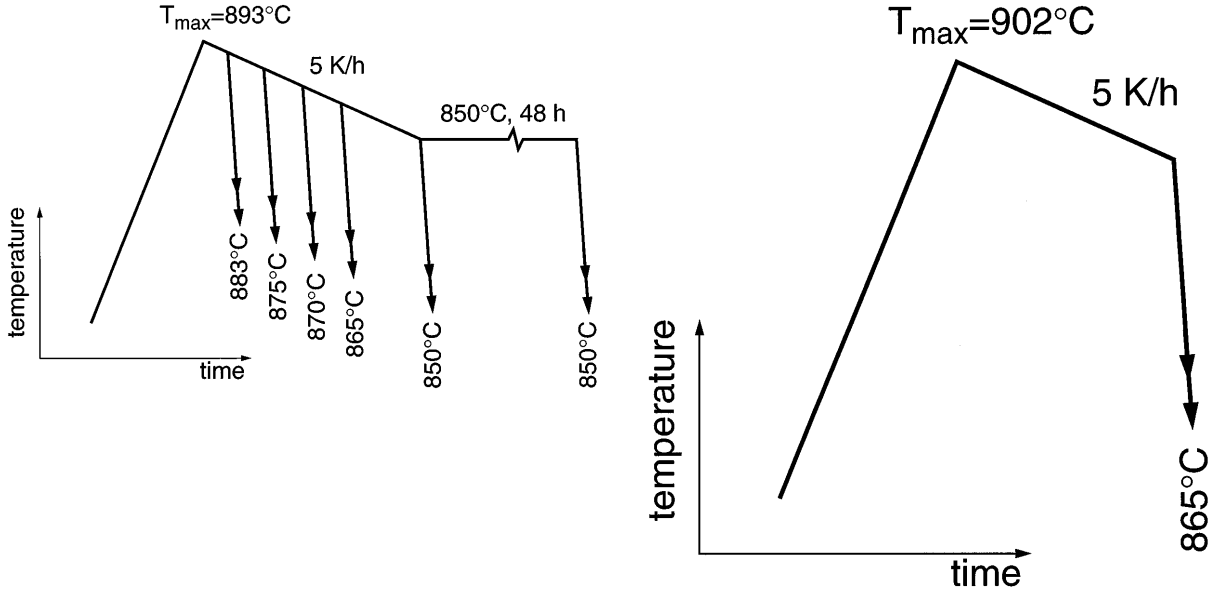


Fig. 1a+b. Heat treatment schedules for the preparation of Bi-2212 thick films (a) and bulk components (b). The double-headed arrows represent the quenching procedures, which were used to freeze the high temperature microstructures.

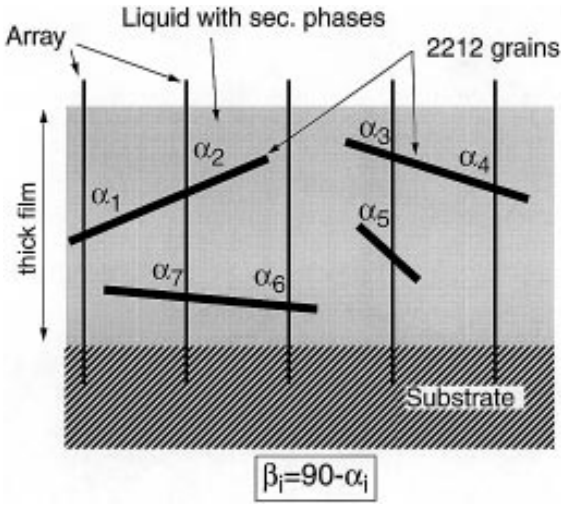


Fig. 2. Assessment of the grain alignment by measuring angles α_i between the a-b-planes of the Bi-2212 grains and an array of lines perpendicular to the substrate at the points of intersection of the array with the grains. In order to get small angles for well aligned grains (i.e. grains almost parallel to the substrate) β_i was calculated by subtracting α_i from 90.

to the substrate. The characterization of the degree of grain alignment of a totally random microstructure consisting of two-dimensional platelets will, therefore, lead to an overestimation of the well-aligned grains compared to the misaligned grains.

3. Results

3.1. Thick Films

In order to understand the formation of the textured microstructure in Bi-2212 thick films it is necessary to investigate the whole evolution of the microstructure from the partially molten state, where no Bi-2212 grains are present anymore, all the way to the final microstructure consisting of more than 90 vol% of Bi-2212. During this period the Bi-2212 grains nucleate and grow and the final microstructure is formed.

At high temperatures ($T > T_{solidus}$), the microstructure of a Bi-2212 thick film that was partially melted under pure oxygen on a silver substrate comprises two solid phases floating in a liquid matrix as it was published elsewhere [23]. These solid phases are either Cu-free with the stoichiometry $Bi_9Sr_{11}Ca_5O_x$ (hereinafter referred to as 91150) or Bi-free with the stoichiometry $Sr_{8.5}Ca_{5.5}Cu_{24}O_y$ (or 014*x*24). During slow cooling at 5 K/h from the maximum temperature of 893°C, the Bi-2212 grains nucleate and grow at $T \leq 875$°C directly from the melt. Thereby most of the peritectic phases are consumed. The solid peritectic phases must dissolve in the liquid in order to provide the needed cations for the Bi-2212 formation. Furthermore, oxygen has to diffuse into the sample from the atmosphere, because the partially melted state is oxygen deficient compared to the solid Bi-2212 phase. Figure 3 shows a detail of the cross section of a thick film, which was melted at 893°C, slowly cooled to 875°C at a rate of 5 K/h and quenched from that temperature. The black grains are the Bi-free phase 014x24, the gray grains are Cu-free. The non-crystalline solidified liquid appears in a slightly brighter gray than the Cu-free 91150 phase. Bright spots are silver precipitates. In the lower middle of the picture, an arrow indicates a Bi-2212 grain which starts growing. This single Bi-2212 platelet probably nucleated at the surface of the 014x24 grain. However, no indications were found, that nucleation happened preferably at one of the solid peritectic phases, the film surface or at the interface to the silver substrate. The bright ''clouds'' in the cross section were mainly observed close to the Cu-free and the Bi-2212 grains. Even if the lateral dimensions of these areas are too small for reliable quantitative EDS,

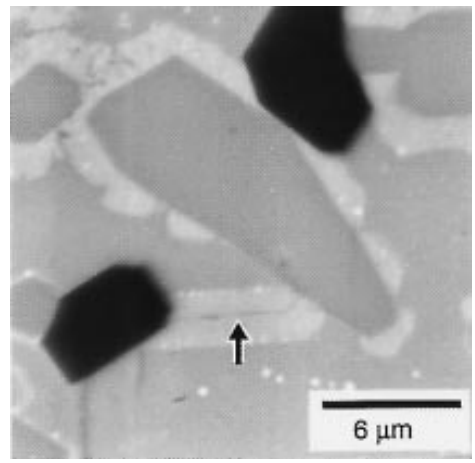


Fig. 3. Micrograph of the cross section of a Bi-2212 thick film which was partially melted at 893°C, slowly cooled at a rate of 5 K/h to 875°C, and quenched from that temperature. The black grains are Bi-free, the grey grains Cu-free. Bright spots are silver precipitates. The arrow indicates a Bi-2212 grain which nucleated at the surface of the Bi-free grain. The origin of the bright ''clouds'' around the Bi-2212 grain and the Cu-free phase is discussed in the text.

Table 1. EDS measurements of the liquid phase and the bright cloud surrounding a Bi-2212 grain in the sample melted at 893°C, cooled slowly at 5 K/h to 875°C and quenched from that temperature. The values are given in No. of cations

	Bi	Sr	Ca	Cu	Ag
liquid	2.32	1.73	0.56	1.23	0.40
bright cloud	2.38	1.78	0.54	1.10	0.29

such measurements were performed. Table 1 compares the as measured EDS-data of the matrix phase and the bright clouds. In general, the bright areas have a higher Bi- and Sr-content but are poorer in Ca and Cu than the rest of the matrix. The reliability of the Ag-content is questionable because of the high amount of silver precipitates close to the evaluated region. The liquid has a composition close to the one-layer compound $Bi_{11}Sr_9Cu_5O_x$ (or *Bi*-11905). A layer containing excess Bi and Sr but less Ca and Cu is formed around a growing Bi-2212 grain when growing out of a melt that has a composition close to Bi : Sr : Ca : Cu = 2 : 2 : 0 : 1. The Cu-free grain dissolving in the liquid leads to a Bi- and Sr-rich layer around the disappearing grain as well. Phases with a high Bi-content appear bright in the SEM if back-scattered electrons are used for imaging, resulting in the mentioned ''clouds''.

In order to find out if the Bi-2212 nuclei have a preferential orientation at the moment of nucleation, the sample melted at 893°C, slowly cooled to 875°C and then quenched was further analyzed. Figure 4 shows a section of the thick film, where several Bi-2212 grains are at an early stage of growth. The arrows show Bi-2212 grains growing in various directions indicating that nucleation is random.

If the slow cooling ramp from the maximum processing temperature is continued to temperatures below 875°C, the randomly oriented Bi-2212 grains grow and more nuclei are formed. The evolution of the Bi-2212 grain alignment during the slow cooling period from the maximum temperature 893°C to 850°C is shown in Fig. 5. In this plot the relative number of Bi-2212 grains of three different samples quenched from three temperatures during the slow cooling ramp is plotted against the angle between substrate and grain. A perfect texture with the c-axis of all grains perpendicular to the substrate would lead to a value of 100% grains misoriented between 0–10 degrees (the sum of all y-values of the same curve is 100%). A completely random orientation of the grains would result in a line having a reduced slope compared to the curve of a well-aligned microstructure. Since the well-aligned grains are overestimated compared to the misaligned grains, the curve of a randomly oriented microstructure will not be horizontal!

The results show a higher degree of alignment with decreasing quench temperature. Grains in the film cooled at 5 K/h from 893°C to 875°C were growing in all directions, indicating that orientation of the Bi-

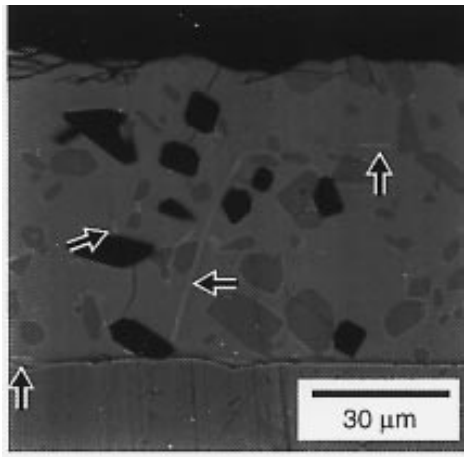


Fig. 4. Randomly oriented Bi-2212 platelets in their early growth state. Arrows indicate Bi-2212 grains which are growing in various directions.

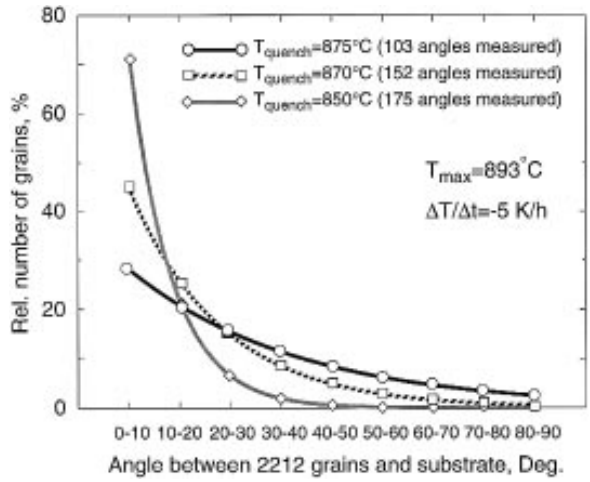


Fig. 5. Change of the Bi-2212 grain alignment during slow cooling from 893°C to 875°C, to 870°C, and to 850°C at a rate of 5 K/h. The y-axis denotes the relative number of grains oriented with their a-b-planes in an angle bi to the substrate. The sum of the measured values of each curve is normalized to 100%.

2212 nuclei is random. With decreasing quench temperature during slow cooling the number of misoriented grains decreased and the overall alignment became better.

The obtained results shown in Fig. 5 can be compared with the model of texture formation proposed by Aksenova et al. [14] and the one by Ray et al. [17] which can be summarized as follows:

1. The crystallization space is quasi two-dimensional.
2. The nuclei of the Bi-2212 grains are disposed homogeneously with random orientation.
3. The initial nucleus concentration does not change.
4. The Bi-2212 platelets grow quasi two-dimensionally.
5. The growth of a Bi-2212 grain is stopped as soon as it hits the sample boundaries or another Bi-2212 grain.

The evolution of the microstructure using these assumptions was simulated graphically. 18 nuclei were distributed in a cross section of a thick film having an aspect ratio of 1 : 5. The coordinates of the nuclei as well as their angle to the substrate were calculated by a random-number generator. However, it was made sure that the orientation of the nuclei was random. These nuclei grew two-dimensionally at a constant rate until they reached an obstacle, where growth stopped. The degree of texture during growth was measured with the same technique used in Fig. 5 and explained in Fig. 2. The result of this simulation is shown in Fig. 6. The degree of texture was determined at three arbitrarily chosen times: ''time = 0'' means shortly after nucleation, when the Bi-2212 platelets are small and do not interact with each other, ''time = 1'' is after some growth of the platelets and ''time = 2'' is chosen at the moment when all Bi-2212 platelets have reached an obstacle and can not grow any longer. From the parameters of the simulation it is clear that the nuclei were randomly oriented. The method used to quantify the degree of grain alignment, however, overestimates the well-aligned grains compared to misaligned platelets. Therefore, the curve belonging to ''time = 0'' is not horizontal but has a negative slope. More important is the fact that the texture does not change quantitatively with time from ''time = 0'' to ''time = 2'' as it was experimentally observed in the melt-processed samples as shown in Fig. 5. We conclude that the model proposed by Aksenova et al. [14] and Ray et al. [17] is basically correct but still too simple to explain al real

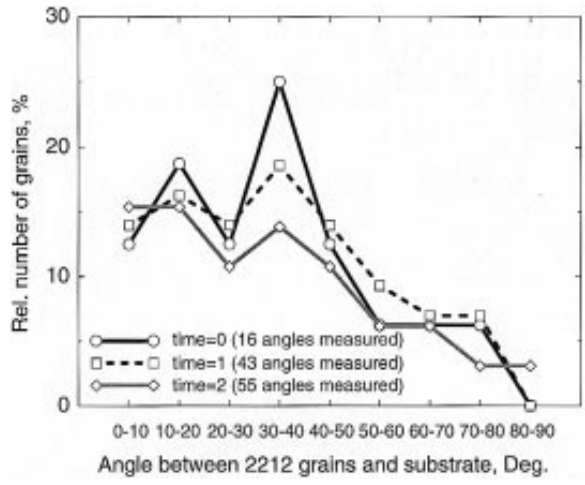


Fig. 6. Angular distribution of Bi-2212 grains growing in a thick films under assumption of the model proposed by Aksenova et al. [14]. The evolution of microstructure was simulated and the degree of grain alignment was measured using the same technique as in Fig. 5.

events occurring during solidification of a Bi-2212 thick film. There are more relevant mechanisms taking place during melt-processing of Bi-2212.

Upon growth, the Bi-2212 platelets may collide with several different obstacles, e.g. solid peritectic phase grains floating in the liquid, the sample surface, the oxide/silver interface, or other Bi-2212 grains. Surprisingly, the solid peritectic grains do not represent an obstacle for the growth of the Bi-2212 grains; the Bi-2212 platelets manage perfectly to find a way between these grains or even cut through them. This is shown in Fig. 7. This sample was partially melted at 893°C, slowly cooled at a rate of 5 K/h to 870°C, and quenched from 870°C. In the middle of the picture a black grain of the $0\underline{14}x\underline{24}$ phase is divided in three parts by the growing Bi-2212 platelets. A possible mechanism leading to such a grain separation will be discussed later.

When a growing Bi-2212 grain or grain bundle approaches the film surface or the interface to the silver, it either stops growing or it changes its growth direction. Figure 8 shows Bi-2212 grains that reached the film surface where they stopped growing. Figure 9 shows an example of Bi-2212 grains which approach the oxide/silver interface under an angle of $\approx 45^\circ$ and turn their growth direction parallel to the substrate. Both pictures were taken from the sample that was partially melted at 893°C, slowly cooled at a rate of

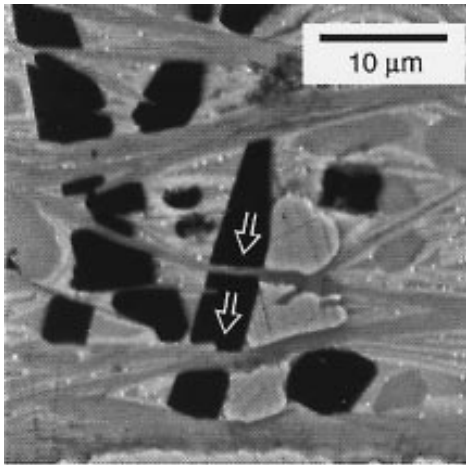


Fig. 7. Cross section of a Bi-2212 thick film which was partially melted at 893°C, slowly cooled at a rate of 5 K/h to 870°C, and quenched from that temperature. A Bi-free grain is divided in three parts by two Bi-2212 platelets (arrows).

5 K/h to 870°C, and finally quenched from that temperature.

The situation gets more complicated when the volume fraction of the Bi-2212 becomes high and the Bi-2212 platelets themselves represent an obstacle for other growing Bi-2212 grains. In this case several different mechanisms were observed. The marked grain in Fig. 10 shows a Bi-2212 platelet that stopped growing on one side as soon as it reached another

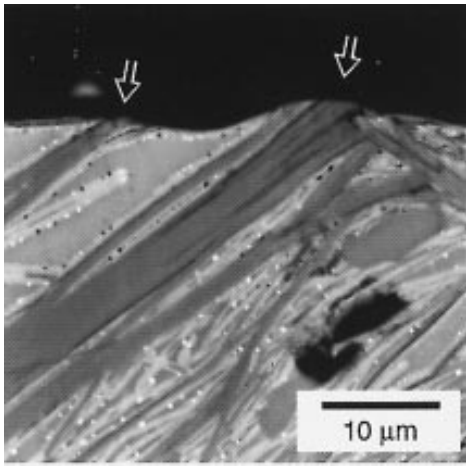


Fig. 8. Cross sectional view of the surface of a Bi-2212 thick film which was partially melted at 893°C, slowly cooled at a rate of 5 K/h to 870°C, and quenched from that temperature. Those Bi-2212 platelets reaching the film surface stopped growing (arrows).

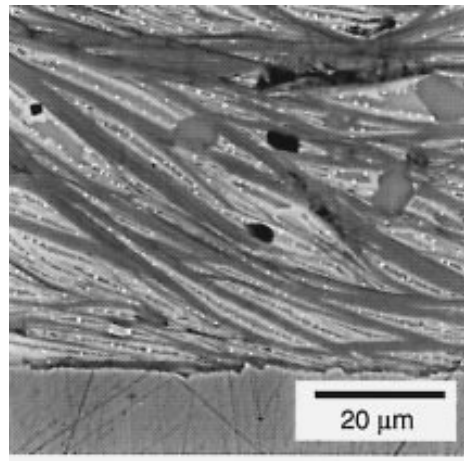


Fig. 9. Cross sectional view of the oxide/silver interface of a Bi-2212 thick film which was partially melted at 893°C, slowly cooled at a rate of 5 K/h to 870°C, and quenched from that temperature. The Bi-2212 grains that approach the substrate change their direction of growth.

Bi-2212 grain. On the other side of the platelet a second mechanism is observed: Two grains colliding under a small angle keep growing together until they reach the next obstacle, in this case the film surface. A third mechanism is documented in Fig. 11: Two Bi-2212 grains seem to cross each other, or one grain grows through the other. A possible mechanism leading to such an arrangement will be discussed later.

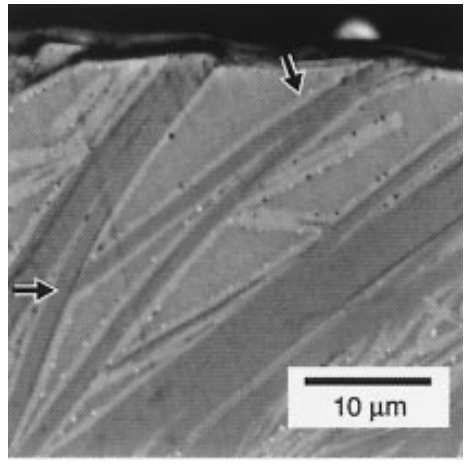


Fig. 10. Cross sectional view of the surface of a Bi-2212 thick film which was partially melted at 893°C, slowly cooled at a rate of 5 K/h to 870°C, and quenched from that temperature. On the left side the marked grain stopped growing when it reached the larger Bi-2212 platelet. On the right side two grains combine under a small angle and keep growing together until they reach the next obstacle (film surface).

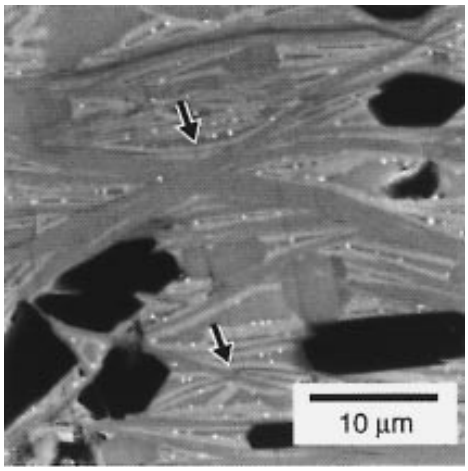


Fig. 11. Cross section of a Bi-2212 thick film which was partially melted at 893°C, slowly cooled at a rate of 5 K/h to 870°C, and quenched from that temperature. The arrows mark two regions where Bi-2212 platelets cross each other.

Obviously, almost all growing Bi-2212 platelets are curved and not perfectly planar. However, Bi-2212 grains with their main growth direction parallel to the substrate can grow to a large size up to several hundred of micrometers.

3.2. *Bulk Samples*

The mechanism that leads to a textured microstructure in partial melt-processed Bi-2212 thick films must be consistent with the microstructure found in bulk samples. Thick samples (d = 1 mm) were melt-processed and their microstructures investigated.

Figure 12 shows the inner part of the bulk sample with a thickness of 1 mm that was partially melted at 902°C, slowly cooled at a rate of 5 K/h to 865°C, and finally quenched from that temperature. The microstructure consists of several phases. The black grains are the Bi-free 0$\underline{14}$x$\underline{24}$-phase. The grains of the Cu-free 9$\underline{11}$50-phase are hardly visible, the Bi-2212 platelets are the meandering grains. Between these solid grains there is still amorphously solidified liquid left.

The Bi-2212 platelets are arranged in bundles of similarly oriented grains. Such bundles are 50–100 μm thick and about 500 μm long. The orientation of the bundles themselves is random throughout the whole cross section. In bulk samples Bi-2212 grains are locally aligned, but show no long range order.

Completely different results, which were published earlier [24], were found when Bi-2212 powder was heated in air to 960°C in an alumina crucible and cooled at a rate of 420 K/h to room temperature. Figure 13 shows the microstructure of such a sample. Due to the increased cooling rate no Bi-2212 but only the one-layer compound (Bi-$\underline{11}$905) was formed upon cooling. In contrast to the Bi-2212 grains observed in

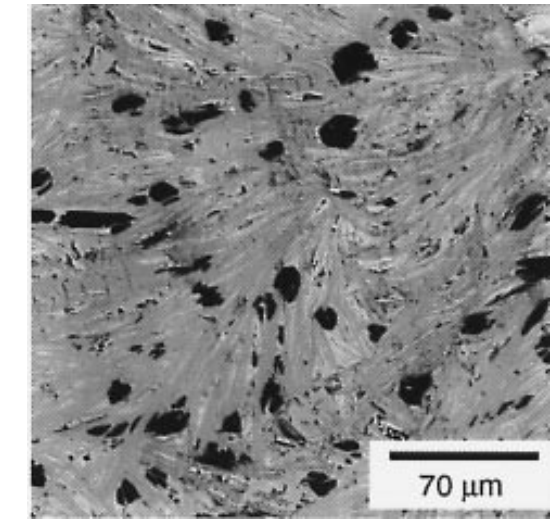


Fig. 12. Inner part of a bulk sample that was partially melted at 902°C, slowly cooled at a rate of 5 K/h to 865°C, and finally quenched from that temperature. The microstructure consists of several phases: Bi-free 0$\underline{14}$x$\underline{24}$-phase (black), Cu-free 9$\underline{11}$50-phase (gray), Bi-2212 platelets. Between these solid grains there is still amorphously solidified liquid left. The Bi-2212 grains are arranged in bundles with a common c-axis but no overall grain alignment relative to the substrate is observed.

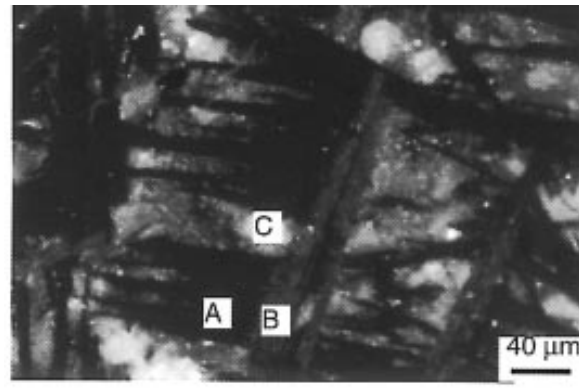


Fig. 13. Microstructure of a Bi-2212 sample that was heated in air to 960°C and cooled at a rate of 420 K/h to room temperature. A: 11905 platelets, B: Bi-free phase (01x1), C: liquid. The $\underline{11}$905-platelets (one-layer compound) nucleated at the Bi-free second phase [18] and grew under an angle of 90° to the surface of the Bi-free grain.

this work, the 11905 grains started growing perpendicularly from the surface of the Bi-free peritectic phase into the melt.

4. Discussion

4.1. Nucleation

In the analyzed cross sections of quenched thick films and bulk samples of this work no indications were found that the Bi-2212 grains preferably nucleated at the sample surface, the interface to the silver substrate or one of the solid peritectic phases, during slow cooling from the partially molten state. It remains unclear where the Bi-2212 grains nucleate. However, from the observations made in polished cross sections of quenched thick films and bulk samples it is clear that in a first stage at least some of the grains of the solid peritectic phases act as heterogeneous nuclei.

If nucleation and growth of the Bi-2212 grains would occur first at the surface of a thick film, as it was proposed by Hasegawa et al. [12], the formation of a textured microstructure with the grains parallel to the surface could easily be explained: The alignment of the top layer would be continued towards the inside of the thick film.

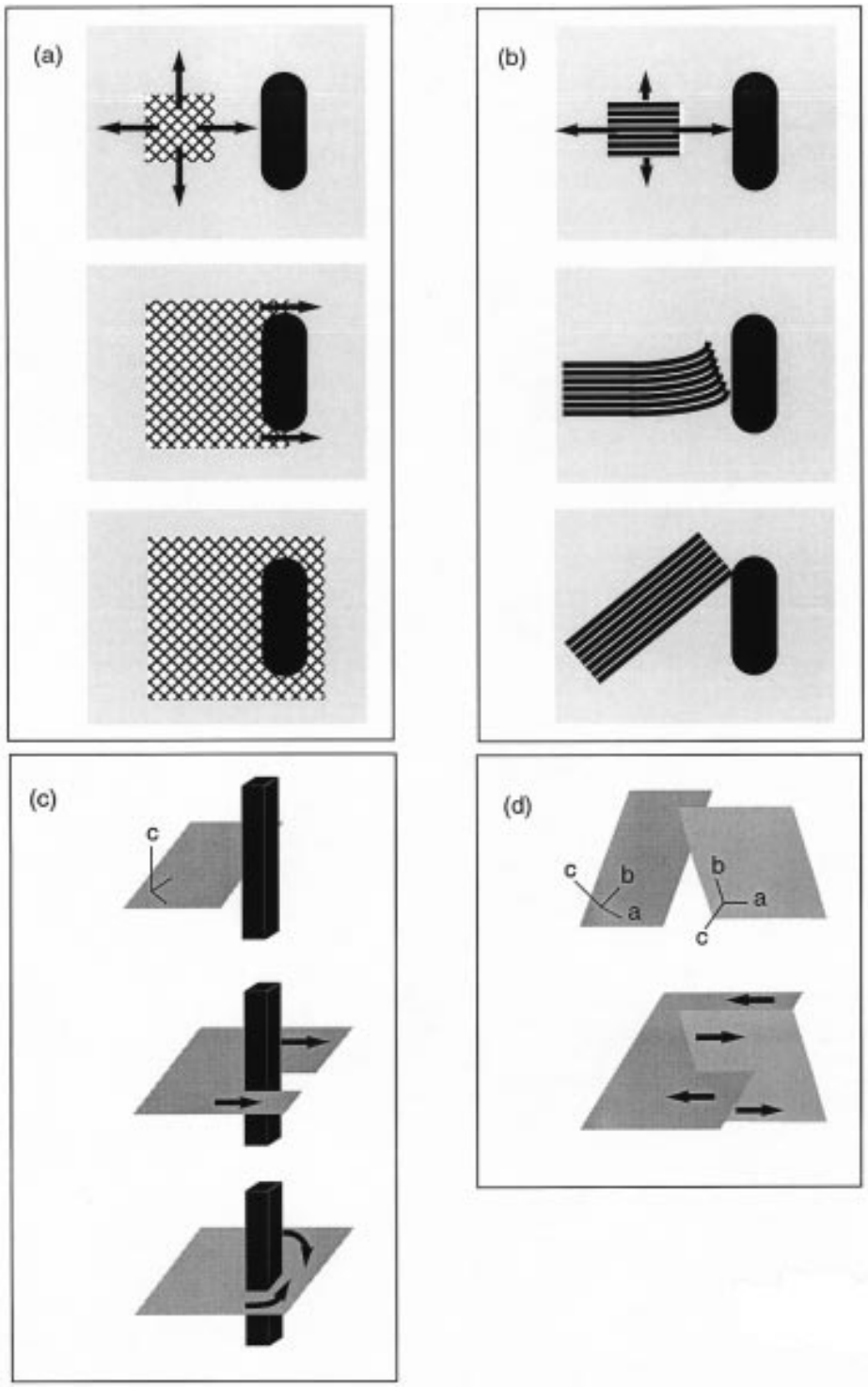
4.2. Grain Alignment

The real mechanism leading to a textured microstructure in melt-processed Bi-2212 thick films and tapes consists of several different mechanisms of nucleation, grain growth and interactions between grains with other grains or the sample boundaries. We have observed the following mechanisms in solidifying Bi-2212 thick films:

I. Bi-2212 grains nucleate at random orientations in the whole cross section of the films at no preferred nucleation sites.
II. The Bi-2212 grains grow upon cooling and new grains are nucleated.
III. When Bi-2212 grains reach a sample boundary (i.e. the film surface or the oxide/silver interface) the growth either stops or the grains bend and change their direction of growth.
IV. The Bi-2212 platelets can grow around a solid obstacle such as the Bi-free or the Cu-free peritectic phases or even cut it.
V. When a Bi-2212 platelet reaches another Bi-2212 grain it either stops growing, changes its growth direction parallel to the other grain or ''cuts'' through the grain.

In Fig. 5 we have shown that the overall grain alignment becomes better during the slow cooling period from the maximum processing temperature. In Fig. 6 we have shown, that the mechanisms proposed earlier do not consider this fact and therefore are too simplifying. From the list above mechanisms II, III, and V have the potential to increase grain alignment. However, in the quenched samples we often observed, that adjacent grains are often parallel as it is seen in Figs. 8–12. A mechanism is proposed, which allows one small grain to turn itself into a favorable orientation. An isotropically growing grain can grow in any direction and an obstacle can be avoided easily as shown in Fig. 14a by growing around the obstacle without distortion. In the case of an anisotropic structure like Bi-2212, the mechanism is different. The growth in c-direction is much slower than in the a-b-planes, leading to the platelet- or mica-like grain morphology. If such a platelet reaches an obstacle and wants to pass around it, it is very unlikely that the growth in a-b-direction stops and proceeds only in the slow c-direction. Therefore, the grain has to bend as shown schematically in Fig. 14b. However, the bending of the grain requires energy because the macroscopic bending must be compensated by distortions on the atomic scale. This results in a driving force that pushes the grains to remain planar instead of bending. This force can turn the whole platelet in an orientation parallel to the obstacle as long as the platelet is small enough and the movement is not hindered by other grains. This leads to a collective alignment of neighboring grains. In contrast to mechanisms proposed earlier [17], in our model it is not a growing grain that turns a second grain, but the growing grain itself turns.

The mechanism that allows a Bi-2212 platelet to grow through a second phase grain is schematically drawn in Fig. 14c. In general one has to keep in mind, that all microstructural images are two-dimensional pictures of three-dimensional structures. The Bi-2212 platelet approaches the second phase and in a first step grows around this grain. Behind the grain the Bi-2212 platelet closes the gap and in a later step in a process similar to a recrystallization process, the second phase is divided when the Bi-2212 structure increases its degree of perfection and closes the hole formed by the


(a)
(b)
(c)
c
(d)
c
b
a
b
a
c

second phase. A similar process is proposed in the case two Bi-2212 platelets seem to grow through each other. Figure 14d shows how a Bi-2212 grain approaches another platelet with a different orientation. As soon as the grains collide, one platelet or even both keep growing in their a-b-planes. If such an arrangement is cut and polished in the region where these grains overlap and analyzed optically, one has the impression, that one grain grew through the other.

Generally, grains can always grow in the direction where no obstacle is present. But there will always be a driving force to grow where an obstacle hinders further expansion of a platelet.

The mechanisms shown in Fig. 14b–d were observed in solidifying Bi-2212 thick films leading to a textured microstructure at the end of the partial melting process. However, when two Bi-2212 platelets interact, it remains unclear which of both will dominate the process and define the orientation of the grains after the interaction. Basically, the larger grain should dominate. In a thick film which is an almost two-dimensional crystallization space the grains growing parallel to the substrate have the potential to grow to very large sizes of several hundred micrometers. These large grains will play a dominant role during the formation of a textured microstructure, as they will win the competition against smaller, misoriented grains. They will force other grains into a parallel orientation and they divide the crystallization space into regions that are even more two-dimensional.

In melt-processed bulk samples with a thickness of 1000 μm no overall grain alignment was found. Because the sample thickness is larger than the average grain size in a-b-direction (i.e. 100–500 μm), the Bi-2212 grains can grow to large sizes even if they are not oriented parallel to the substrate. The formation of the bundles of collectively oriented Bi-2212 platelets can be explained by the mechanism of grain rotation mentioned above.

5. Summary

The formation of a textured microstructure in Bi-2212 thick films and bulk samples was investigated by quenching such specimens from various temperatures during the partial melt-process and analyzing the cross sections optically. Thick films showed a good overall grain alignment with the c-axis of the Bi-2212 platelets almost perpendicular to the substrate. Bulk samples consisted of bundles of locally aligned Bi-2212 grains but showed no overall texture.

When the originally randomly oriented Bi-2212 grains grow, they encounter various kinds of obstacles as second phase grains, the sample boundaries, or even other Bi-2212 platelets. Several mechanisms were observed how the grains interact with these obstacles and how small grains can adapt their orientation to a neighboring larger grain.

The basic condition of grain alignment in melt-processed Bi-2212 thick films is the combination of the extreme anisotropic grain growth of the mica-like Bi-2212 platelets with the quasi two-dimensional sample geometry. However, several more mechanisms occur during transformation of the partially molten state to an almost single phase Bi-2212 structure.

In bulk samples no geometrical restrictions force the Bi-2212 platelets to grow in a special direction. The sample size is larger than the average grain size. Therefore, the crystallization space is three-dimensional and as a consequence no overall alignment is found in fully processed samples.

Fig. 14a–d. Schematic views of several mechanisms occurring during solidification of isotropic and anisotropic structures. Figure (a) shows for comparison how an isotropically growing crystal (hatched) can avoid an obstacle (black) by growing around it. Figure (b) is a schematic view of an anisotropic layered structure (like Bi-2212) approaching an obstacle (black). The macroscopic growth direction is changed, whereas the growth direction on the atomic scale remains the same (i.e. the a-b-layers). This leads to a bending of the grain requiring energy because of distortions of the atomic lattice. This energy pushes the whole platelet to turn in order to flatten its shape. Figure (c) shows a schematic illustration of a Bi-2212 platelet approaching a second phase grain (top). In a first stage (middle) the Bi-2212 grain grows around the obstacle and closes the gap behind it (bottom). In the last stage the Bi-2212 grain closes the hole produced by the second phase grain and "cuts" it in two parts. Figure (d) is a schematic illustration of a Bi-2212 platelet approaching another platelet with a different orientation. When the growth fronts collide one or even both grains keep growing along their a-b-planes. If such an arrangement is cut and polished in the region where both platelets overlap, and finally analyzed optically, one has the impression that the grains grew through each other.

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References

1. J. Shimoyama, J. Kase, T. Morimoto, H. Kitaguchi, H. Kumakura, K. Togano and H. Maeda, *Jpn. J. Appl. Phys*., **31**, L1167 (1992).
2. D. Buhl, Th. Lang and L.J. Gauckler, *Supercond. Sci. Technol*., **10**, 32 (1997).
3. B. Heeb, D. Buhl, Th. Lang and L.J. Gauckler, *Proc. of 1993 TMS/AMS Materials Week,* Oct. 17–21, 1993, Pittsburgh, USA.
4. Th. Baumann, G. Kemmler and P. Kluge-Weiss, *Proc. of 7th Int. Workshop on Crit. Currents in Superconductivity*, Jan. 24–27, 1994, Alpbach, Austria.
5. J. Kase, N. Irisawa, T. Morimoto, K. Togano, H. Kumakura, D.R. Dietderich and H. Maeda, *Appl. Phys. Lett*., **56**, 970 (1990).
6. J. Shimoyama, N. Tomita, T. Morimoto, H. Kitaguchi, H. Kumakura, K. Togano, H. Maeda, K. Nomura and M. Seido, *Jpn. J. Appl. Phys*., **31**(9B), L1328–L1331 (1992).
7. H. Nonoyama, K. Hayashi, M. Nagata and K.-I. Takahashi, ''Advances in Superconductivity IV'', *Proceedings of the 4th International Symposium on Superconductivity (ISS '91*), October 14–17, 1991, Tokyo, Japan, Eds. H. Hayakawa and N. Koshizuka, Springer Verlag Tokyo, pp. 485–488.
8. Th. Lang, D. Buhl, M. Cantoni and L.J. Gauckler, *Inst. Phys. Conf. Ser. No 148*, Paper presented at Applied Superconductivity, Edinburgh, July 3–6, 1995, IOP Publishing Ltd., 111–114.
9. B. Heeb and L.J. Gauckler, NASA Conference Publication 3290, 1, Proceedings of the Fourth International Conference and Exhibition: World Congress on Superconductivity, Orlando FL, June 27–July 1, 1994, Eds. K. Kristen and C. Burnham, 382–390.
10. Th. Lang, D. Buhl, M. Cantoni, Z. Wu and L.J. Gauckler, *Proc. of 1995 International Workshop on Superconductivity,* Co-sponsored by ISTEC and MRS, June 18–21, 1995, Maui, USA.
11. J. Kase, T. Morimoto, K. Togano, H. Kumakura, D.R. Dietderich and H. Maeda, *IEEE Trans. Mag*., **27**(2), 1254–1257 (1991).
12. T. Hasegawa, H. Kobayashi, H. Kumakura, K. Togano, *Supercond. Sci. Technol*., **7**, 579–582 (1994).
13. T. Hasebe, Y. Tanaka, T. Yanagiya, T. Asano, M. Fukutomi and H. Maeda, *Jpn. J. Appl. Phys*., **31**(1A-B), L21–L24 (1992).
14. T.D. Aksenova, P.V. Bratukhin, S.V. Shavkin, V.L. Melnikov, E.V. Antipova, N.E. Khlebova and A.K. Shikov, *Physica C*, **205**, 271–279 (1993).
15. W. Zhang and E.E. Hellstrom, *Physica C*, **218**, 141–152 (1993).
16. E.E. Hellstrom, *J. Metals*, **44**, 48–53 (1992).
17. R.D. Ray II and E.E. Hellstrom, *Physica C*, **251**, 27–49 (1995).
18. J. Tenbrink, M. Wilhelm, K. Heine and H. Krauth, *IEEE Trans. Mag*., **27**(2), 1239–1246 (1991).
19. S.M. Wecker, P.R. Morris, *J. Appl. Cryst*., **11**, 211–220 (1978).
20. Th. Lang, B. Heeb, D. Buhl and L.J. Gauckler, NASA Conference Publication 3290, 2, Proceedings of the Fourth International Conference and Exhibition: World Congress on Superconductivity, Orlando FL, June 27–July 1, 1994, Eds. K. Kristen and C. Burnham, 753–61.
21. R. Müller, Th. Schweizer, P. Bohac, R.O. Suzuki and L.J. Gauckler, *Physica C*, **203**, 299–314 (1992).
22. P. Majewski, *Adv. Mater*., **6**(6), 460–469 (1994).
23. Th. Lang. D. Buhl, M. Cantoni, B. Hallstedt, D. Risold, S. Al-Wakeel, D. Schneider and L.J. Gauckler, submitted to *Physica C*. (1997).
24. B. Heeb, S. Oesch, P. Bohac and L.J. Gauckler, *J. Mater. Res*., **7**(11), 2948–2955 (1992).