

# Partial Melting of Bulk Bi-2212

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## Abstract

Dense and textured Bi-2212 bulk samples have been produced by the partial melting process. The appropriate amount of liquid phase necessary for complete densification has been adjusted by controlling the maximum processing temperature. The maximum temperature itself has to be adapted to several parameters as powder stoichiometry, silver addition and oxygen partial pressure. Prolonged annealing at 850 and 820 °C and cooling in N<sub>2</sub> atmosphere led to nearly single phase material with T<sub>c</sub>=92 K. Critical current densities j<sub>c</sub> of 2'200 A/cm<sup>2</sup> at 77 K/0 T have been achieved in samples of more than 1 mm thickness. Reducing the thickness below 0.4 mm enhances j<sub>c</sub> considerably to values > 4'000 A/cm<sup>2</sup>. The addition of 2 wt% Ag decreases the solidus temperature of the Bi-2212 powder by 21 °C. Therefore, the maximum heat treatment temperature of Ag containing samples can be markedly lowered leading to a reduction of the amount of secondary phases. In addition, Ag enhances slightly the texture over the entire cross-section and as a result j<sub>c</sub> at 77 K/0 T.

## Introduction

Melt processing of Bi-2212 (Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub>) is a common fabrication technology to produce superconducting devices with a dense, weak-link free microstructure. Various geometries have been produced by this technique: (a) Thick films on Ag-substrates are fabricated by the so-called *partial melting* route [1,2] leading to an excellent grain alignment and high critical current densities at 77 and 4.2 K even in long tapes. (b) Ag sheathed wires are produced by a very similar process [3-5]. So far, good superconducting properties in long lengths have been achieved at temperatures between 4.2 and 25 K. (c) Massive devices, e.g. tubes and rings for current leads and limiters, have been fabricated by *complete melting* at temperatures above 1000 °C. For these geometries, the high temperatures are required to achieve the appropriate viscosity to form the desired shape [6], but they promote oxygen loss during melting and the development of an unfavorable microstructure with coarse secondary phases even after prolonged annealing at temperatures above 800 °C [7-9]. As a consequence, the critical current density at 77 K remains limited. Nevertheless, technical devices are feasible with bulk materials due to components with large cross-section carrying high currents.

The purpose of this study is to apply the partial melting process to produce bulk Bi-2212 material in order to avoid the disadvantages of the complete melting. The heat treatment was optimized in order to enhance the critical current density of massive

devices at 77 K. Since Ag was used as container material, special emphasis was laid on the control of its influence on the processing parameters and the resulting properties.

## Experimental

### a. Powder preparation

Powder with the stoichiometry  $\text{Bi}_{2.2}\text{Sr}_{2.0}\text{Ca}_{1.0}\text{Cu}_{2.0}\text{O}_x$  was prepared by the standard calcination process. The appropriate amounts of  $\text{Bi}_2\text{O}_3^{\text{a}}$ ,  $\text{SrCO}_3^{\text{b}}$ ,  $\text{CaCO}_3^{\text{c}}$  and  $\text{CuO}^{\text{d}}$  were mixed and calcined at 750 °C for 18 h, at 800 °C for 36 h, at 820 °C for 85 h and at 850 °C for 96 h in a flowing gas mixture of 20%  $\text{O}_2$  and 80%  $\text{N}_2$  with intermediate grindings. This powder stoichiometry was chosen, because it is reported to be within the single phase region of Bi-2212 [10]. In addition, the Bi-excess reduces the amount of Bi-free secondary phases of melt processed Bi-2212 [11]. The nearly single phase calcined powder was ball milled in hexan for 2 hours, dried and sieved passing completely the 32  $\mu\text{m}$  sieve. To a part of the calcined powder 2 wt% Ag was added in form of  $\text{Ag}_2\text{O}$ . The  $\text{Ag}_2\text{O}$  powder<sup>e</sup> was mixed with the Bi-2212 powder on a roll mill for 3 h, resulting in a homogeneous mixture of the two powders. The  $\text{Ag}_2\text{O}$  is decomposed during heating leading to finely dispersed Ag particles of a few microns on the 2212 powder particles.

DTA measurements revealed a solidus temperature of the powder of 881 °C in air and 892 °C in oxygen, respectively. The addition of 2 wt% silver led to a decrease of the solidus temperature to 871 °C in oxygen.

To control the quality of the powder a pressed pellet was sintered at 850 °C for 96 h in air and drop quenched in liquid  $\text{N}_2$ . The sample was single phase ( $a=0.541$  nm,  $c=3.086$  nm) and showed a  $T_c$  of 95 K.

### b. Sample preparation and characterization

Pellets with a diameter of 13 mm and variable thickness were uniaxially pressed at a pressure of 150 MPa, put into Ag crucibles and subjected to the heat treatment, which consisted of three main steps:

- Partial melting at 880 to 905 °C for 2 h in oxygen to densify the samples.
- Annealing at 850 °C for 48 h in oxygen after cooling at a cooling rate of 30 °C/h to form a high volume fraction of the 2212 phase [12]. A second annealing step of 80 h at 820 °C in oxygen or air followed.
- Cooling at a rate of 300 °C/h to room temperature; the atmosphere was changed to nitrogen ( $p_{\text{O}_2} \approx 10^{-3}$  atm) at 700 °C in order to optimize the oxygen stoichiometry.

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<sup>a</sup> PCF, 99.9% purity

<sup>b</sup> Solvay Barium Strontium GmbH, > 99.9%

<sup>c</sup> Solvay Barium Strontium GmbH, > 99.9%

<sup>d</sup> Cerac Inc., > 99.8%

<sup>e</sup> Fluka Chemika, > 99.0%

The microstructure of the samples was investigated by light microscopy, X-ray diffraction (XRD) with  $\text{CuK}\alpha$  radiation and Si as internal standard, and scanning electron microscopy (SEM). To achieve information about the microstructure of the entire volume, the sample thickness was reduced by removing material in steps of 100  $\mu\text{m}$  by polishing. Chemical compositions of phases were determined by EDX at an acceleration voltage of 25 kV. The ZAF correction was applied to the intensities of the  $\text{BiM}\alpha$ ,  $\text{SrL}\alpha$ ,  $\text{CaK}\alpha$ , and  $\text{CuK}\alpha$  lines, and the compositions calculated by means of internal standards.

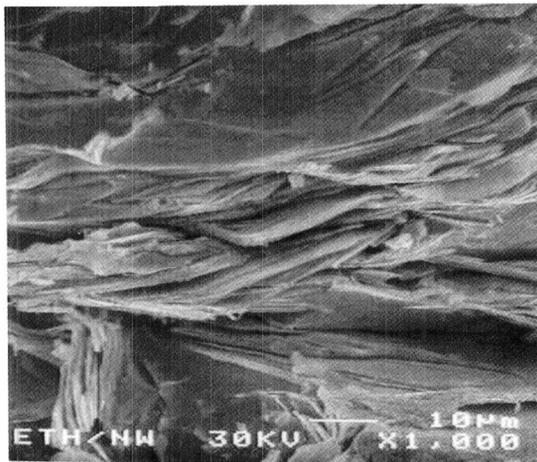
The critical temperature  $T_c$  was determined resistively by the conventional four-probe method or by AC susceptibility. The measurements of the critical current density  $j_c$  were performed magnetically in an AC magnetometer at  $f=4$  Hz using the 1  $\mu\text{V}/\text{cm}$  criterion. The samples were immersed in a bath of liquid nitrogen. The current densities were calculated from the width  $\Delta M$  of the measured  $M(H)$  loops. Since granularity was never found in melt processed Bi-2212 [13]  $\Delta M$  must be due to macroscopic currents only.

## Results and Discussion

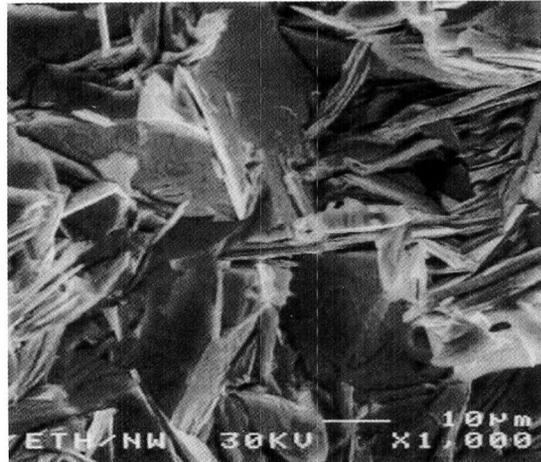
### a. Microstructure

The maximum heat treatment temperature is the crucial processing parameter for the microstructural development of melt processed Bi-2212. For thick films it has been shown that only a narrow temperature range is suitable to achieve dense microstructures with high critical current densities [2,14]. Similar behavior was observed for bulk material. In Figure 1 the fracture cross-section of a sample processed at  $T_{\text{max}}=905$  °C is shown. The typical microstructure of melt processed Bi-2212 consisting of bundles of 2212 grains with parallel c-axis and separated by (001) twist boundaries [13] can be recognized. It is completely dense and no major secondary phases can be detected. SEM observations in the backscattering mode revealed the chemical composition to be very homogenous throughout the cross-section. These findings were further confirmed by XRD showing that only traces of 3430 are present as secondary phase beside the 2212 phase with  $a=0.541$  nm and  $c=3.087\pm 0.002$  nm. The chemical composition of the 2212 phase is  $\text{Bi}_{2.13}\text{Sr}_{2.06}\text{Ca}_{1.06}\text{Cu}_2\text{O}_x$  and is close to the composition of the starting powder.

In contrast to the bulk, both the surface and the interface to the Ag substrate show a considerable amount of secondary phases. At the surface the Bi-free 014x24 phase was found; its appearance is mainly attributed to Bi-loss during processing. At the interface the 2201 and the Cu-free 3430 phase were present as secondary phases. In addition, the very large FWHM ( $0.63^\circ$ ) of the (008) peak of the 2212 phase as well as the EDX analysis showing a chemical composition of  $\text{Bi}_{2.82}\text{Sr}_{2.31}\text{Ca}_{1.03}\text{Cu}_2\text{O}_x$  indicate a high density of 2201 intergrowths inside the 2212 grains. However, the second phase rich layers at the surface and interface have a thickness of less than 100  $\mu\text{m}$ .



*Fig. 1:* SEM picture of the cross-section of a Bi-2212 bulk sample processed at  $T_{\max}=905$  °C.



*Fig. 2:* SEM picture of the cross-section of a Bi-2212 bulk sample processed at  $T_{\max}=880$  °C.

Reducing the maximum processing temperature led to a decrease of the amount of liquid phase and to a dramatically reduced density. Figure 2 shows the fracture cross-section of a sample heated to  $T_{\max}=880$  °C. Only a thin layer of approx. 10 to 20  $\mu\text{m}$  at the Ag interface is molten and densified, whereas the bulk is only sintered and remained porous. Obviously, two solidus temperatures can be found in this sample; affected by the Ag substrate, Bi-2212 near the interface begins to melt at a markedly lower temperature than the rest of the sample. However, the small amount of liquid phase produced is inadequate to promote the densification of the entire sample. Therefore, a processing temperature exceeding the solidus temperature by about 15 °C is considered to be appropriate for complete densification of bulk Bi-2212, even in Ag crucibles. This difference is larger than the 3-7 °C reported for thick films [2,14].

As mentioned earlier, doping  $\text{Bi}_{2.2}\text{Sr}_2\text{CaCu}_2\text{O}_x$  with 2 wt% Ag decreases the solidus temperature by 21 °C to 871 °C in oxygen atmosphere. Taking into account that the proper amount of liquid phase can be achieved by the previously mentioned 15 °C above solidus, the maximum temperature of the partial melting process was reduced to 885 °C. Indeed, this low temperature led to the complete densification of the samples and to a considerably smaller amount of secondary phases, especially of the Bi-free  $\text{014x24}$  at the surface and 2201 at the Ag/Bi-2212 interface.

In Figure 3 the melting behavior of Bi-2212 on Ag substrates as a function of the partial melting temperature is summarized. Without Ag addition (figure 3a) a temperature around 905 °C is necessary for complete densification of the sample. At this temperature, the surface is overheated and the Ag/Bi-2212 interface suffers a substantial Bi-loss leading to an enhanced volume fraction of secondary phases in these layers. As it will be shown later, these layers are the most textured ones and so possible regions of high current carrying capacity. Therefore, an improvement of the melting process in regard of the microstructural development of surface and interface seems to be advantageous for the enhancement of the current density.

Lowering the maximum processing temperature  $T_{\max}$  to 880 °C does not solve the problem. The microstructure of the interface layer is certainly improved, but the amount of liquid phase is insufficient to densify the whole sample. Therefore, such low temperatures can only be used for the fabrication of thick films which consist entirely of Ag/Bi-2212 interface. The second, more promising way to improve the microstructure of bulk material is the addition of 2 wt% Ag to the powder (figure 3b). It lowers the solidus temperature of the entire sample and eliminates the inhomogeneous melting. At the same time, the processing temperature is comparable to the one used for the partial melting of thick films. Therefore, the volume fraction of secondary phases at the interface due to overheating and at the surface due to Bi evaporation can be markedly reduced.

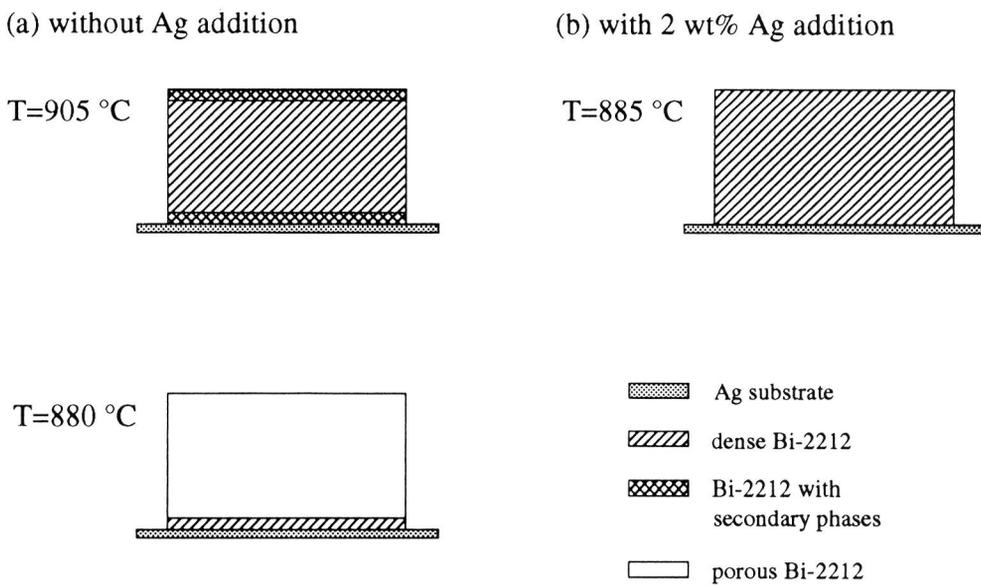


Fig.3: Schematic drawing of the melting behavior of Bi-2212 bulk samples on Ag substrates (a) without and (b) with 2 wt% Ag addition.

## b. Texture

Figure 4 shows the dependence of the degree of texture<sup>a</sup> on the distance from the Ag/Bi-2212 interface. The high value of  $f=0.99$  at the interface expresses an almost perfect alignment of the (ab)-plane parallel to the Ag substrate. However, the highly textured layer has only a thickness of less than 100  $\mu\text{m}$ . Comparable good grain alignment is found at the sample surface.

<sup>a</sup> Quantification of the texture from XRD measurement:  $f = \frac{\sum \text{Intensities}(001)_{2212}}{\sum \text{Intensities}(hkl)_{2212}}$

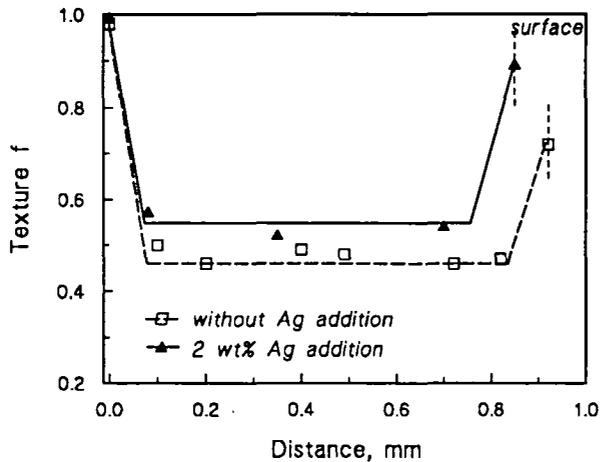


Fig.4: Degree of texturing from the Ag/Bi-2212 interface to the surface of melt processed Bi-2212 with and without Ag addition

The degree of texturing in the bulk is lower, but constant over the entire cross-section. The parameter  $f$  showing values of 0.5 lays markedly above the value of an unoriented powder specimen with  $f=0.14$  and a little above  $f$  of a pressed and sintered specimen ( $f=0.47$ ). This indicates that a considerable degree of texture in the bulk is already formed by pressing which is intensified by the partial melting process. Excellently textured layers are induced by the Ag substrate as well as by the free surface. The Ag addition slightly enhances the degree of alignment over the entire cross-section.

### c. Properties

Table 1 shows the critical temperatures  $T_c$  of melt processed and sintered Bi-2212. All heat treatment schedules including partial melting lead to the same  $T_c$  of 92 K. This temperature is somewhat lower than  $T_c = 95$  K of the sintered and drop quenched sample without Ag addition, but equal to the  $T_c$  of sintered Bi-2212 with 2 wt% Ag addition. This indicates, that the oxygen stoichiometry of the partially molten Bi-2212 is well adjusted, but  $T_c$  is slightly lowered due to the influence of Ag taken up from the substrate during partial melting and/or added to the starting powder.

Heat treatment	Ag addition, wt%	$T_c$ , K
Partial melting	--	91.5 - 92
	2	92
Sintering	--	95
	2	92

Table 1: Dependence of  $T_c$  on heat treatment conditions and Ag addition

The critical current density  $j_c$  being the most important design parameter of system components was determined at 77 K, the envisaged operating temperature. Figure 5 shows the  $j_c$  dependence on the sample thickness  $d$  after partial melting in oxygen and annealing at 850 °C in oxygen as well as at 820 °C in air. The maximum processing

temperature was 905 °C for pure Bi-2212 samples and 885 °C for Ag containing samples. For sample thicknesses  $d \leq 0.4$  mm  $j_c$  increases strongly with decreasing sample thickness. Values above 4'000 A/cm<sup>2</sup> can be reached. For samples with  $d > 0.4$  mm the dependence of  $j_c$  on component dimensions is much reduced but still present. Critical current densities larger than 2'000 A/cm<sup>2</sup> can be obtained in specimens of more than 1 mm thickness after this process.

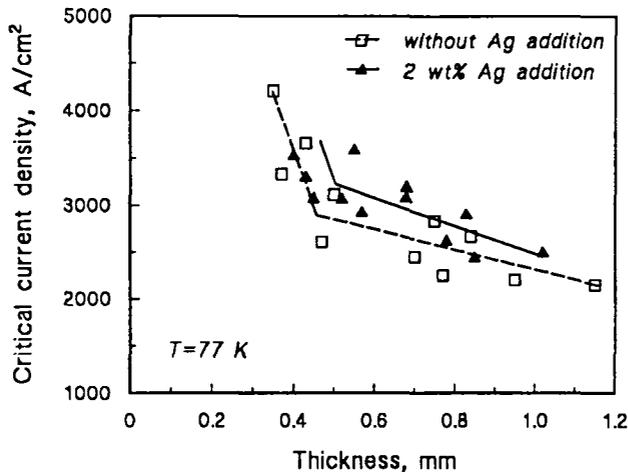


Fig.5: Dependence of  $j_c$  (77 K/0 T) on sample thickness for partially molten Bi-2212 with and without Ag addition (incl. air annealing)

The Ag addition enhances  $j_c$  for all sample sizes. Since  $T_c$  of all samples is equal, we conclude that the increase is connected with the improved microstructure, namely phase composition and texture.

Assuming that self-field effects can be neglected at the present sample size of  $d < 1.2$  mm,  $j_c$  is mainly influenced by the phase composition and texture. As we have shown before, the samples are nearly single phase and the texture is constant over the main part of the cross-section. Therefore, the increase of  $j_c$  with decreasing thickness might be attributed to the increasing contribution of the highly aligned layer at the Ag/Bi-2212 interface with decreasing overall sample thickness.

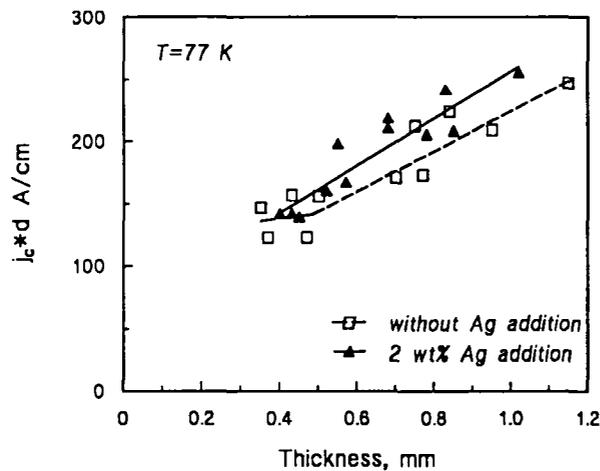


Fig.6: Dependence of  $j_c \cdot \text{thickness}$  (77 K/0 T) on sample thickness for partially molten Bi-2212 with and without Ag addition (incl. air annealing)

Figure 6 shows the dependence of the product  $j_c \cdot d$  on sample thickness. This product is of interest for technical devices. It gives an indication how much current can be transported in a conductor of a certain width. The increase of  $j_c \cdot d$  with increasing sample thickness is remarkable and the maximum has not been reached with  $d=1.2$  mm. This behavior clearly demonstrates that bulk Bi-2212 is well suited for high current applications. The loss of critical current density can be over-compensated by increasing the thickness. For comparison, the best thick films have  $j_c > 10^4$  A/cm<sup>2</sup> [2,14], but their  $j_c \cdot d$  is in the region of 30-40 A/cm, almost an order of magnitude smaller than in bulk material.

In Figure 7 the thickness dependence of  $j_c$  of the samples with the final annealing at 820 °C in oxygen instead of air (figure 5) is shown. Again, the maximum processing temperature was 905 °C for pure Bi-2212 samples and 885 °C for Ag containing samples for samples annealed in O<sub>2</sub> at 820 °C.

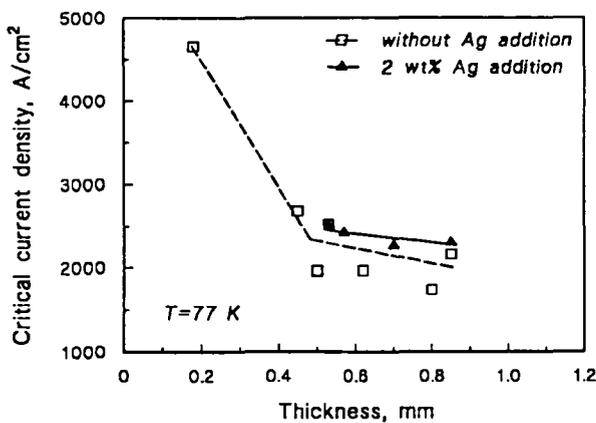


Fig.7: Dependence of  $j_c$  (77 K/0 T) on sample thickness for partially molten Bi-2212 with and without Ag addition (oxygen annealing)

The critical current density for all sample thicknesses is significantly reduced. Since macroscopic differences like  $T_c$ , texture or phase compositions cannot be observed, the influence of the oxygen annealing is not understood so far. More careful investigations of the micro- and nanostructure is necessary to explain the advantage of air annealing. Of course, the lower  $j_c$  values lead also to lower  $j_c \cdot d$  as illustrated in figure 8.

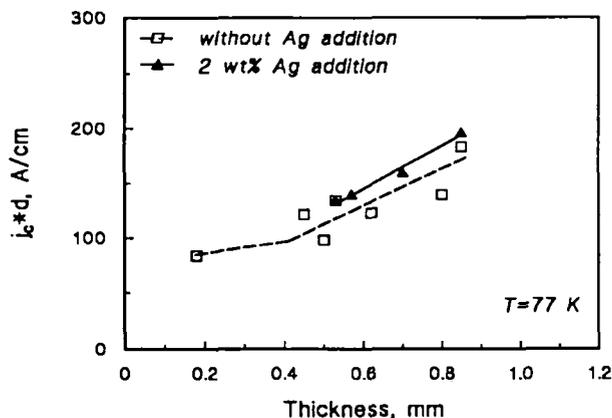


Fig.8: Dependence of  $j_c \cdot d$  (77 K/0 T) on sample thickness for partially molten Bi-2212 with and without Ag addition (oxygen annealing)

## Conclusions

Partial melting is an appropriate processing technology to produce dense bulk Bi-2212 with nearly single phase microstructures. It leads to a considerable texture over the entire cross-section. A particularly pronounced degree of grain alignment is found at the Ag/Bi-2212 interface and the surface. Therefore, avoiding secondary phases in this layer enhances the current density in thin samples ( $d < 0.4$  mm), in which the interface layer contributes substantially to the total current. The addition of 2 wt% Ag is shown to be a useful measure for this purpose.

The maximum processing temperature has to be approx. 15 °C above the solidus temperature in order to achieve a sufficient amount of liquid phase promoting the densification of the sample. Annealing including a step at 820 °C in air is superior to annealing only in oxygen atmosphere. Cooling in N<sub>2</sub> is sufficient to obtain a high T<sub>c</sub>. No further heat treatment is necessary to adjust the oxygen stoichiometry.

Critical current densities  $j_c$  (77 K/0 T) above 4'000 A/cm<sup>2</sup> are achieved for a sample thickness  $d < 0.4$  mm. The addition of 2 wt% Ag enhances  $j_c$  slightly. Increasing the thickness leads to a reduction of  $j_c$ . However, because the thickness dependence becomes small for  $d > 0.4$  mm, bulk Bi-2212 with high critical currents can be produced by partial melting .

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