The Role of Silver in the Processing and Properties of Bi-2212

Th. Lang, B. Heeb, D. Buhl and L.J. Gauckler

Nichtmetallische Werkstoffe, ETH Zürich, Sonneggstrasse 5, CH-8092 Zürich

Abstract

The influence of the silver content and the oxygen partial pressure on the solidus temperature and the weight loss during melting of $Bi_2Sr_2Ca_1Cu_2O_x$ has been examined by means of DTA and TGA. By decreasing the oxygen partial pressure the solidus is lowered (e.g. $\Delta T = 59°C$ by decreasing pO_2 from 1 atm to 0.001 atm) and the weight loss is increased. The addition of silver causes two effects: (a) the solidus is further decreased (e.g. 2wt% Ag lower $T_{solidus}$ by up to 25°C, depending on the oxygen partial pressure), (b) the weight loss during melting is reduced.

Thick films (10-20 µm in thickness) with 0 and 5 wt% silver and bulk samples with 0 and 2.7 wt% silver were melt processed in flowing oxygen on a silver substrate in the DTA, allowing the observation of the melting process and a good temperature control. The critical current densities are vigorously dependent on the maximum processing temperature. The highest j_c in thick films (8000 A/cm^2 at 77 K, 0 T) was reached by melting 7°C above the solidus temperature. The silver addition shows no significant effect on the processing parameters or the superconducting properties.

The highest j_c for bulk samples (1 mm in thickness) was obtained by partial melting at 900°C or 880°C, depending on the silver content of the powder (0 or 2.7 wt%). The j_c of the samples is slightly enhanced from 1800 A/cm^2 (at 77 K, 0 T) to 2000 A/cm^2 by the silver addition.

To be able to reach at least 80% of the maximum critical current density, the temperature has to be controlled in a window of 5°C for thick films and 17°C for bulk samples.

Introduction

Silver is of great importance for the preparation of superconducting Bi-Sr-Ca-Cu-oxide, because of several advantageous properties: (a) It was found to be nonpoisonous to the superconducting properties of Bi-2212 [1-3], (b) Silver shows a high oxygen diffusivity [2-5] so that the oxygen uptake through a silver sheath is possible, (c) Bi-2212 tapes melt processed on silver are highly a/b textured [6-10], (d) Silver lowers the processing temperatures of Bi-2212 thick films [11], (e) its ductility enables the production of tapes and wires through a powder-in-tube process [12], still providing a sufficient mechanical stabilization.

These reasons make silver the preferred material to surround the Bi-Sr-Ca-Cu-O compound, especially when the samples are prepared by a process involving a reactive liquid phase. Such a process is the partial melting process, which was shown to be suitable to reach high critical

current densities in Bi-2212 thick films [13-14] and bulk samples [15-16]. Therefore, it is interesting to know how the silver substrate or a silver addition influences the processing parameters of such compounds.

The aim of this study was to evaluate the influence of silver additions on the solidus temperature and the weight loss during melting of Bi-2212 and to examine the influence of the maximum processing temperature during the partial melting on the critical current density of thick films and bulk samples.

Experimental

a. Powder preparation

Powders with the stoichiometry $Bi_2Sr_2Ca_1Cu_2O_x$ and $Bi_{2.2}Sr_{2.05}Ca_{0.95}Cu_2O_x$ were prepared by the standard calcination process. The appropriate amounts of Bi_2O_3[A], $SrCO_3$[B], $CaCO_3$[C] and CuO[D] were mixed and calcined in MgO- or Ag-crucibles at 750°C, 800°C and 820°C with intermediate grindings. Finally they were pressed into pellets, sintered for 150 h at 850°C in air and ground again. XRD measurements showed the powders to be nearly single phase.

Mixtures of Bi-2212 with silver (0-15.4 wt%) were prepared by adding appropriate amounts of Ag_2O powder[E], mixing for 3 h in a ball mill and decomposing the silver oxide at 600°C. After this treatment the silver was distributed homogeneously over the whole batch as metallic particles with diameters of a few μm.

The melting behavior of Bi-2212 with silver additions up to 15.4 wt% was investigated by means of *differential-thermal-analysis* (DTA) and *thermal-gravimetry* (TGA). 100 mg of Bi-2212 powder with different Ag contents were heated in Al_2O_3 crucibles with 5°/min to 1000°C in three different atmospheres: (a) oxygen[F] (pO_2=1 atm), (b) air (pO_2=0.21 atm), (c) nitrogen[F] (pO_2≈0.001 atm).

b. Sample preparation

Thick films

The thick films were prepared by drying a butanol suspension of Bi-2212 (cation-ratio 2.2:2.05:0.95:2) with 0 and 5 wt% silver in silver forms. The partial melting of these samples was carried out in the DTA.

The heat treatment consisted of the following steps:

- heating with 1°/min to T_{max} ($868°C \leq T_{max} \leq 897°C$)
- cooling to 850°C with 5°/h
- cooling to room temperature with 5°/min

The whole heat treatment was done in flowing oxygen.

To adjust the oxygen content of the Bi-2212 and therefore the T_c, the films were post-annealed in flowing nitrogen ($pO_2 \approx 0.001$ atm) at temperatures below 600°C. The final thickness of the films was 10-20 μm, the diameter 11 mm.

Bulk

Bulk samples with a diameter of 13 mm and a final thickness of 1 mm were prepared by pressing the Bi-2212 powder (cation ratio 2.2:2.05:0.95:2) with 0 and 2.7 wt% Ag uniaxially into silver cups with a pressure of 150 MPa. This silver amount was chosen, because it was measured after processing a Bi-2212 pellet without Ag addition by the partial melting process on a Ag substrate to be uptaken by the superconductor from the substrate.

The heat treatment for bulk samples differed from the one for thick films and consisted of the following steps:

- heating with 1°/min to T_{max} ($865°C \leq T_{max} \leq 918°C$)
- holding T_{max} for 2 h
- cooling to 850°C with 40°/h
- annealing at 850°C for 12 h
- cooling to room temperature with 5°/min

This part of the heat treatment was performed in the DTA. In order to reach an almost single phase microstructure [17], the samples were post-annealed for 72 h at 850°C. Both, the melting and the annealing were done in flowing oxygen. To control the oxygen stoichiometry and therefore the T_c of the samples, the atmosphere was switched to nitrogen ($pO_2 \approx 0.001$ atm) at 700°C during cooling to room temperature.

c. Characterization

The measurements of the critical current densities were performed in an AC magnetometer at f=4-10 Hz using the 1 μV/cm criterion. The samples were immersed in a bath of liquid nitrogen during the measurement. The current densities were calculated using the width of the measured M(H) loops.

Results and Discussion

a. DTA/TGA measurements

Figure 1 shows the dependence of the solidus temperature $T_{solidus}$ of Bi-2212 on the silver content at three different oxygen partial pressures. Besides the well known fact, that the melting is shifted towards lower temperatures for decreasing oxygen partial pressures, the measurements show a drop of the solidus with silver additions for all oxygen partial pressures. In oxygen as well as in air, $T_{solidus}$ reaches a minimum at approximately 2 wt% Ag addition. Silver contents of more than 5 wt% lead to no further change. The maximum temperature drop due to the silver is reduced with decreasing oxygen partial pressures and comes to 25°C in oxygen, 20°C in air and 10°C in nitrogen.
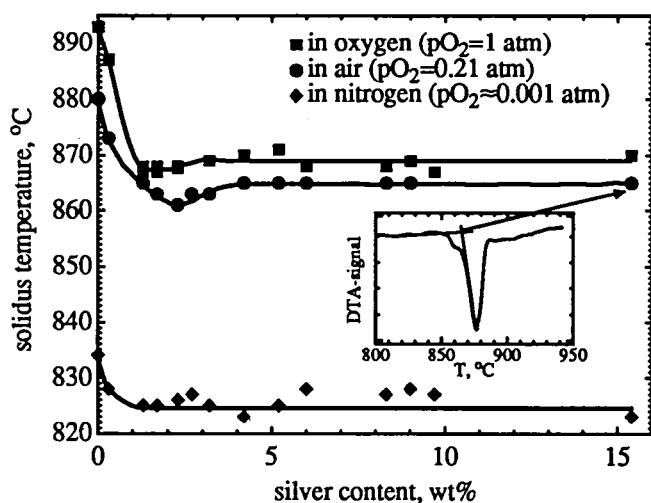

Fig. 1: Influence of silver addition and oxygen partial pressure on the solidus temperature of Bi-2212. The inset shows how the solidus temperatures were determined from the DTA data.

During melting, Bi-2212 releases oxygen to the atmosphere, leading to a loss of weight. Figure 2 shows the TGA curves of Bi-2212 without any added silver at three different oxygen partial pressures (1, 0.21 and 0.001 atm). A strong weight loss is observed as soon as the solidus temperature is exceeded. It is obvious, that the Bi-2212 releases more oxygen in low oxygen containing atmospheres. At $pO_2 \approx 0.001$ atm the weight loss comes to 1.5 wt% of the initial amount of powder, at $pO_2 = 1$ atm it is about 1 wt%. The kink in the TGA measurement in oxygen, which was observed in all measurements in this atmosphere with varying evidence, cannot be explained ultimatively. It may be related to the formation and decomposition of a solid phase, which is stable only at higher oxygen partial presssures (e.g. the O14x24 phase), during the peritectic melting.

The loss of oxygen during melting is found to be dependent on the silver content of the Bi-2212 powder, as shown in figure 3, where the weight loss of the oxide in the temperature range between the solidus temperature $T_{solidus}$ and ($T_{solidus}$+100°C) is plotted as a function of the silver content. Here again the behavior in three different oxygen partial pressures is investigated. Despite the scattering of the measurements, a trend towards lower weight losses with increasing silver contents is visible. This effect being pO_2-dependent is most pronounced in oxygen ($pO_2 = 1$ atm) and least in nitrogen ($pO_2 \approx 0.001$ atm). Kanai *et al* [18] presume the Ag to be liquid at the partial melting temperatures in the presence of Bi-2212, and the liquid metal to accomodate released oxygen in the melt process. Taking into account that the oxygen solubility of

liquid Ag is enhanced with increasing oxygen partial pressure, the results obtained in this work confirm their assumption.
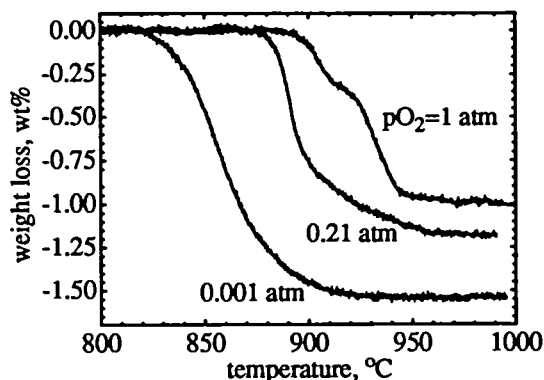

Fig. 2: TGA curves of Bi-2212 without silver additions showing the weight loss during melting. The solidus temperatures (determined from the DTA data), are 834°C, 880°C and 893°C for the measurement at pO_2=0.001 atm, 0.21 atm and 1 atm, respectively.
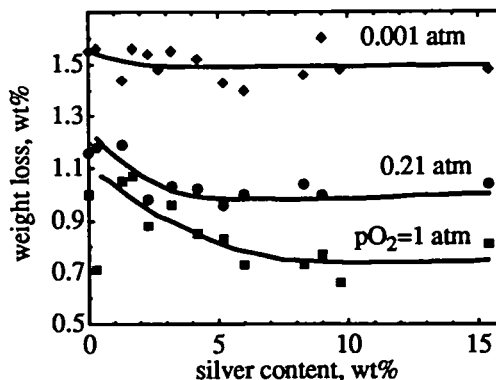
Fig. 3: Weight loss of Bi-2212 as a function of the silver content and the oxygen partial pressure in the temperature range $T_{solidus}$ to $(T_{solidus}+100°C)$.

b. Partial melting of Bi-2212 thick films

The maximum processing temperature during the partial melting strongly influences the superconducting properties of Bi-2212. Figure 4 shows the dependence of the critical current density (at 77 K, 0 T; $1\mu V/cm$-criterion) on the maximum temperature during the heat treatment combined with a typical DTA curve of a Bi-2212 thick film on a silver substrate. The DTA data reveal a solidus temperature of 873°C, being significantly lower than the measured 886°C for the powder in Al_2O_3 crucibles. Therefore, the Ag substrate influences the melting behavior of the Bi-2212 thick film considerably.
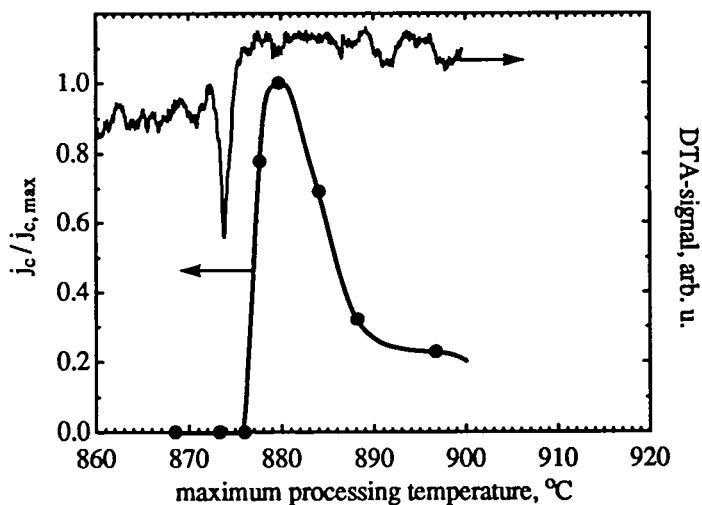

Fig. 4: Influence of the maximum processing temperature on the critical current density of Bi-2212 thick films.

The upper left curve shows the DTA peak of the melting of a film.

The critical current densities of the thick films show a narrow maximum at about 880°C, corresponding to 7°C above the solidus temperature. If T_{max} is chosen below or only a little above the solidus ($T_{max} \leq 876$°C), no or not enough liquid phase is produced to densify the sample. By processing the thick film at a temperature exceeding the solidus more than 15°C, coarse secondary phases lead to a decrease of j_c. Therefore, to reach high critical current densities in thick films the processing temperature has to be controlled within 5°C.

The j_c of thick films is very sensitive on the heat treatment or, more precisely, on the temperature difference between the melting of the sample and the maximum processing temperature. Thus, it is not possible to declare a specific T_{max} to be the best to produce high j_c thick films, because $T_{solidus}$ is influenced by many parameters: the atmosphere, the substrate material, doping elements, powder stoichiometry and so on. A thick film on a MgO substrate heat treated with $T_{max}=880$°C (the most promising temperature to produce thick films on silver) would not show high critical current densities, because the $T_{solidus}$ of Bi-2212 on magnesia is about 886°C and, therefore, no liquid phase would appear to densify the material. In consideration of these facts, it is more reasonable to regard $\Delta T = T_{max} - T_{solidus}$ and not T_{max} as crucial processing parameter.

Figure 5 shows the result of the same experiment as above but carried out with 5 wt% silver added samples in comparison with the results without silver addition. The maximum j_c of both, silver free and silver added Bi-2212, is the same (8000 A/cm^2 at 77 K, 0 T). However the curve for the silver added samples is shifted slightly towards lower temperatures. The width of the processing window promoting high j_c remains unchanged.

Since no major difference in the $j_c(T_{max})$ behavior of pure and Ag added Bi-2212 thick films is observed, we conclude that the film thickness of 10-20 μm and the high diffusivity found for silver in Bi-2212 [19] allow chemical interactions between the superconductor and the substrate. Thus, there is no significant difference in the solidus temperature of thick films whether the silver is present as substrate or added to the powder.
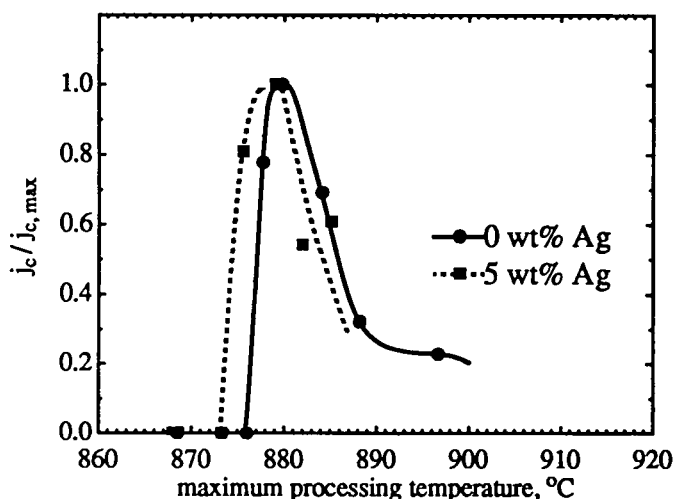

Fig. 5: Dependence of j_c on the maximum process temperature of thick films with 0 and 5 wt% silver. The maximum j_c for both samples is 8000 A/cm^2 (77 K, 0 T; 1μV/cm-criterion)

c. Partial melting of bulk samples

A typical DTA curve and the critical current densities in dependence of the maximum temperature T_{max} of the pure Bi-2212 bulk samples are plotted in figure 6. The DTA curve shows two

major peaks (marked as 1 and 2). The low temperature peak (1) is attributed to the melting of the Bi-2212 at the interface with the silver. Peak 2 represents the melting of the rest of the sample, which is not in contact with the silver substrate. It agrees well with the $T_{solidus}$ of Bi-2212 in Al_2O_3 crucibles.

As shown before for Bi-2212 thick films, the critical current densities depend on T_{max}, having a maximum of 1800 A/cm^2 (at 77 K, 0 T) at 900°C. This temperature exceeds the solidus temperature of the pellet (marked as T_s in figure 6) by 12°C. The temperature window to produce bulk samples with a high j_c is markedly broader than for thick films.

The melting behavior of the bulk sample clearly shows, that it can be considered to be composed of a silver influenced region close to the substrate and the bulk, which is not affected by the silver substrate. To achive high critical current densities, the optimum processing temperature has to be adjusted to the melting of the *bulk*. Since the Ag substrate does not influence this part of the sample, the temperature lays as high as 900°C. Lowering T_{max} in order to adjust it to the melting of the interface is detrimental for the densification of the sample. The amount of liquid is insufficient leading to a porous microstructure with low j_c. However, the high processing temperature is unvavorable for the microstructure and properties of the Ag affected interface (c.f. figure 4). The interface is overheated, contains a high amount of secondary phases and does not contribute distinctively to the current density of the whole sample. This is particularly undesirable because the interface is the most textured part of the sample [16] with a good current carrying potential.
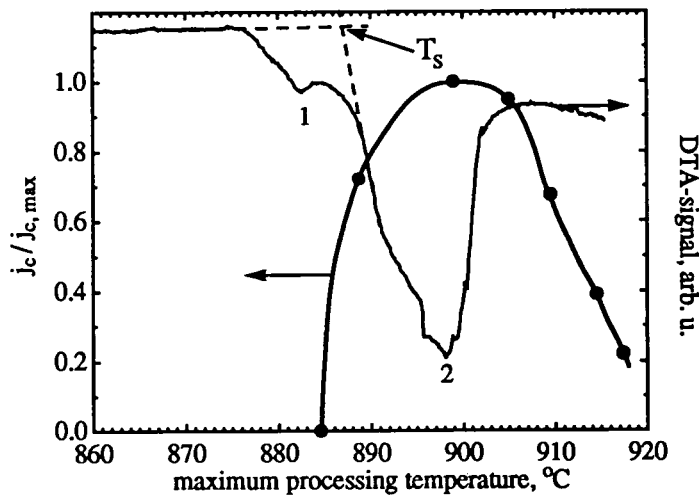

Fig. 6: Influence of the maximum processing temperature on the critical current density of Bi-2212 bulk samples in silver crucibles.
The second curve is a typical DTA measurement of such a sample, where two distinct peaks can be seen. Their origin is explained in the text.

The overheating of the interface should be avoided using silver doped Bi-2212 powder. In this case the interface of the pellet being in contact with the silver substrate does not melt at lower temperatures than the rest of the sample. The DTA curve of a pellet with 2.7 wt% Ag shows only one peak with an onset temperature of 864°C, confirming the homogenous melting of the entire sample. Figure 7 compares the results of the j_c measurements of the Ag-added and the Ag-free samples as a function of the processing temperature. The Ag addition shifts the dome significantly towards lower temperatures (ΔT=10-15°C) and enhances the maximum current density from 1800 A/cm^2 without silver to 2000 A/cm^2 in the silver containing samples. The optimum processing temperature for Ag added bulk (880°C) lays in the range of the temperatures leading to high critical current densities of thick films. Therefore, it is adjusted to the

melting of the *bulk and the interface* leading to excellent phase purity of the entire sample and an enhanced j_c (77 K).
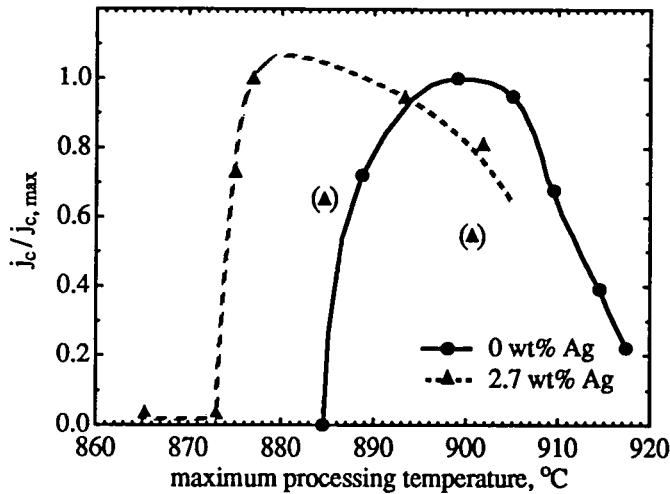

Fig. 7: Dependence of j_c (77 K, 0 T) on the maximum processing temperature of bulk samples with 0 or 2.7 wt% Ag. The maximum critical current densities are 1800 A/cm^2 for the silber free and 2000 A/cm^2 for the silver added samples.
The points in brackets result from samples, which lost some of the liquid phase during the melt processing through the silver substrate.

To explain the enhancement of j_c (77 K) due to the Ag addition, we can make a simple calculation with the following assumptions: The Ag/Bi-2212 interface is regarded as well-textured thick film with a thickness of 20 μm and j_c of 10^4 A/cm^2 for T_{max}=880°C and of 1800 A/cm^2 for T_{max}=900°C. The thickness of the bulk should be 980 μm, its j_c 1800 A/cm^2. It is now possible to compare the critical current density of a sample with an overheated interface (T_{max}=900°C) and a sample with a good interface (T_{max}=880°C). It results, that by keeping the processing temperature low enough to reach an interface free of secondary phases and therefore high local j_c, the j_c of the entire sample can be enhanced by about 10%. This indeed is the increase measured in this work by adding silver to the Bi-2212 powder and by processing at lower temperatures.

Summary

The melting behavior of Bi-2212 with silver additions up to 15.4 wt% in different oxygen partial pressures was inverstigated by means of DTA and TGA. The results show, that the addition of 2 wt% Ag lowers the solidus of Bi-2212 by up to 25°C, depending on the atmosphere. Silver contents exceeding 5 wt% cause no further change of $T_{solidus}$. The weight loss during melting, which is related to a oxygen loss of the compound, is decreased by melting in high oxygen partial pressures and by adding silver.

Thick films (d=10-20 μm) and bulk samples (d=1 mm) with and without silver additions were melt processed on silver substrates in the DTA. In thick films, the highest j_c was reached by melting 7°C above the solidus temperature of the film ($T_{solidus}$=873°C). The critical current density depends strongly on the maximum process tempearture, which has to be controlled within a window of about 5°C. An addition of 5 wt% Ag to the thick film lowers the process temperatures slightly (2°C) and does not enhance j_c. The physical properties of the thick films are mainly influenced by the silver substrate and, therefore, additional silver has hardly any further effects.

Bulk samples show a broader dependence of j_c on the maximum process temperature than the thick films. Temperature variations of ±7°C still lead to a high j_c (>80% of $j_{c,max}$). The addition of 2.7 wt% silver leads to significantly lower processing temperatures and an enhancement of the critical current density. The enhancement is attributed to the improved microstructure of the Ag/Bi-2212 interface.

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