Tape Casting and Partial Melting of Bi-2212 Thick Films

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Abstract

To produce Bi-2212 thick films with high critical current densities tape casting and partial melting is a promising fabrication method. Bi-2212 powder and organic additives were mixed into a slurry and tape casted onto glass by the doctor blade tape casting process. The films were cut from the green tape and partially molten on Ag foils during heat treatment.
We obtained almost single-phase and well-textured films over the whole thickness of 20 μm. The orientation of the (a,b)-plane of the grains was parallel to the substrate with a misalignment of less than 6 °. At 77K/0T a critical current density of 15'000 A/cm^2 was reached in films of the dimension 1cm x 2cm x 20μm (1μV/cm criterion, resistively measured). At 4K/0T the highest value was 350'000 A/cm^2 (1nV/cm criterion, magnetically measured).

Introduction

For applications in electrical engineering, superconducting devices with macroscopic dimensions are required. This asks for other fabrication techniques and processing parameters than for thin films, sputtered polycrystalline films or single crystals. According to today's knowledge textured polycrystalline material is suitable for operations of large currents.
Melt-processing of Bi-2212 produces a dense, almost single-phase microstructure with no weak-link behavior [1]. The appropriate superconducting properties (T_c, T_{irr}, j_c) are achieved by controlling the processing parameters during melting, solidification and post annealing [2]. Particularly the critical current density can be further increased in thick films by grain alignment.
Kase et al. [3] first reported that tape casting and partial melting is a promising method to fabricate highly textured Bi-2212 thick films on Ag-substrates up to 10 μm thickness. Improvements of their processing lead to high critical current densities up to 3.2 x 10^4 A/cm^2 (77K/0T) and 5.9 x 10^5 A/cm^2 (4.2K/0T) [4].
The exact controlling of the processing parameters for partial melting and annealing is crucial, since the single-phase region is a function of temperature, oxygen partial pressure and cation stoichiometry [4] and an aligned microstructure is achieved only by the appropriate cooling [5].
Today, the applications of Bi-2212 thick films tend to low temperatures and high transport currents. Reproducable high critical current densities of thick films at 77K without

Ag as a parallel conductor are scarcely reported yet. The relation between properties and microstructure has not been clarified yet.
In this paper, we report processing procedures to fabricate textured Bi-2212 thick films on Ag-substrates by tape casting via the partial melting route. Emphasis is laid on the parameters enhancing the critical current densities and their reproducibility at 77K, as well as on the correlation between the properties and the microstructures of the tapes.

Experimental

Powder calzination
The starting materials (Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO) were weighed in the desired stoichiometry of $Bi_{2.2}Sr_{2.05}Ca_{0.95}Cu_2O_x$ which is in the centre of the single-phase region of Bi-2212. The powder was calcined at temperatures from 750 to 820 °C for 24 to 72 hours with intermediate grindings. This resulted in a powder consisting mainly of Bi-2212 containing small amounts Bi-2201 and Bi-free 014x24 as secondary phases. The grain size of the powder was smaller than 32 μm.

Tape casting
The Bi-2212 powder was mixed with organic additives into a non-toxic slurry. The organic formulation consisted of solvent (ethanol), dispersant (triolein), plasticizer (polyethylene glycol and phtalic acid ester) and binder (polyvinyl butyral). The slurry was milled for 4 hours, degassed and cast into tapes by the doctor blade tape casting process. The green tapes were 1.5 m long and 15 cm wide. The thickness of the tapes was 100 μm and shrank to 50 μm during drying. Samples of the desired shapes were cut from the green tape, put on silver foils (50 μm thick) and subjected to the heat treatment. The thickness of the tapes after the heat treatment was 20 μm.

Heat treatment
The heat treatment consisted of 4 main steps. First, the organic additives used for the tape casting process were burned out by heating slowly to 500 °C and holding there for 10 hours. The second, crucial step was the partial melting. The samples were heated at 40 °C/h to the maximum temperature (870 - 890 °C) and then cooled down with 5 °C/h to the annealing temperature of 850 °C. During this step the material was densified, the grains were aligned and the Bi-2212 phase formed. This part of the heat treatment was done in O_2 or air. The third step was the annealing of the samples at 850 °C in O_2. This is known to influence both, microstructure and properties, of Bi-2212 ceramics.The last step after cooling down to room temperature was a reduction treatment at temperaturers below 600 °C in flowing N_2 ($p(O_2) < 10^{-3}$ atm) to adjust the oxygen content of the samples.
The processing parameters of the heat treatment were varied to investigate the influence of the processing on the properties and the microstructure. The maximum temperature was changed in small steps from clearly below the (870 °C) to high above the solidus temperature (895 °C). Additionally, the partial melting was done in air adjusting the tem-

peratures to the lower solidus temperature (minus 20 °C compared to O_2). The annealing at 850 °C in O_2 was prolonged up to 100 hours. The reduction treatment was done at different temperatures between 400 and 600 °C in N_2 for 2 to 25 hours.

Sample characterization
To determine the superconducting properties the samples were magnetically measured by vibrating sample magnetometer (VSM) and AC-susceptometer. The critical temperature and the irreversibility temperature were determined by extrapolation of the reversible and the irreversible magnetization (VSM) or the real and the imaginary part of the susceptibility(AC). The critical current density was calculated from the width of the hystersis loop of M(H) (VSM). As we never found any granularity in melt-processed Bi-2212, ΔM is purely due to macroscopic intergranular currents [7]. It was measured from 4 to 90 K. Additionally, the critical transport current and its dependence on applied magnetic fields was measured resistively by the four-point dc method. The microstructure was investigated by light microscopy, X-ray diffraction analysis with CuK_α radiation and Si as internal standard, and scanning electron microscopy. Chemical compositions of phases were determined by energy dispersive X-ray diffraction.

Results and discussion

a) Microstructure

The thickness of the final Bi-2212 layer is approximately 1/3 of the green tape thickness. Fig.1 shows the fractured cross-section of a melt processed tape with the oxide thickness of 20 μm. The highly aligned microstructure, which is formed during the slow cooling from the partially molten state, is attributed to the Ag substrate and the low oxide layer thickness < 30 μm. The Bi-2212 layer is composed of stacks of plate-like grains with the aspect ratio exceeding 50. The XRD patterns confirm the good texture of the films; only the *(00l)* reflections of the Bi-2212 phase are observed (inset in fig.2). The misalignment of the grains is estimated from rocking curves of XRD measurements to be < 6° (fig.2).

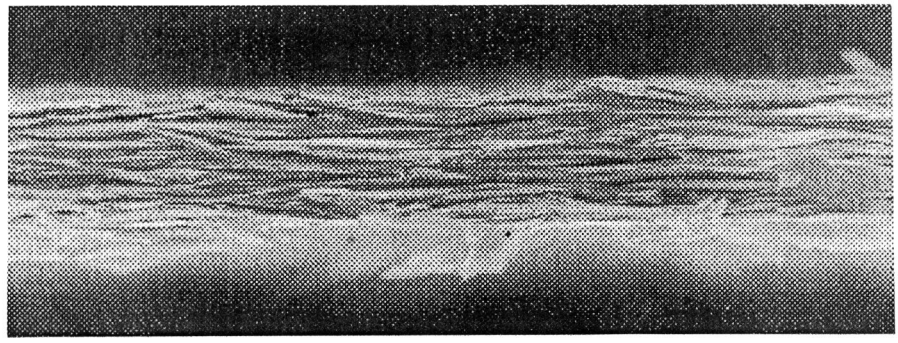

Fig.1 cross-section of a partially molten Bi-2212 thick film with a homogenous thickness of 20μm.

Influence of maximum processing temperature

Fig. 2 shows as well the strong influence of the maximum processing temperature on the phase composition of the thick films. Partial melting 5 °C above the solidus temperature results in nearly single-phase Bi-2212. The secondary phases are the one-layer Bi-2201, the Bi-free phase of the stoichiometry $Sr_{14-x}Ca_xCu_{24}O_y$ and the Cu-free phase $Bi_3Sr_4Ca_3O_z$. Partial melting 10 °C above the solidus temperature increases the amount of secondary phases. Increasing the maximum processing temperature to 15 °C above the solidus temperature increases the amount of secondary phases. The Bi-2201 phase becomes the main phase besides 2212 grains with a high density of 2201-intergrowths. From the asymmetric broadening of the *(008)* and *(0012)* reflections of the Bi-2212 phase the amount of these intergrowths can be calculated [8].

Light microscopy investigations show that the Bi-free 014x24 phase has the shape of needles, independent of the processing temperature. For processing temperatures more than 10 °C above the solidus temperature the length of the needles grows from less than 20 µm to over 200 µm. The Cu-free 3430 phase appears as cubes (length < 5 µm) for processing temperatures lower than 10 °C above solidus. At higher temperatures, large stalks of 3430 (length > 200 µm) are visible.

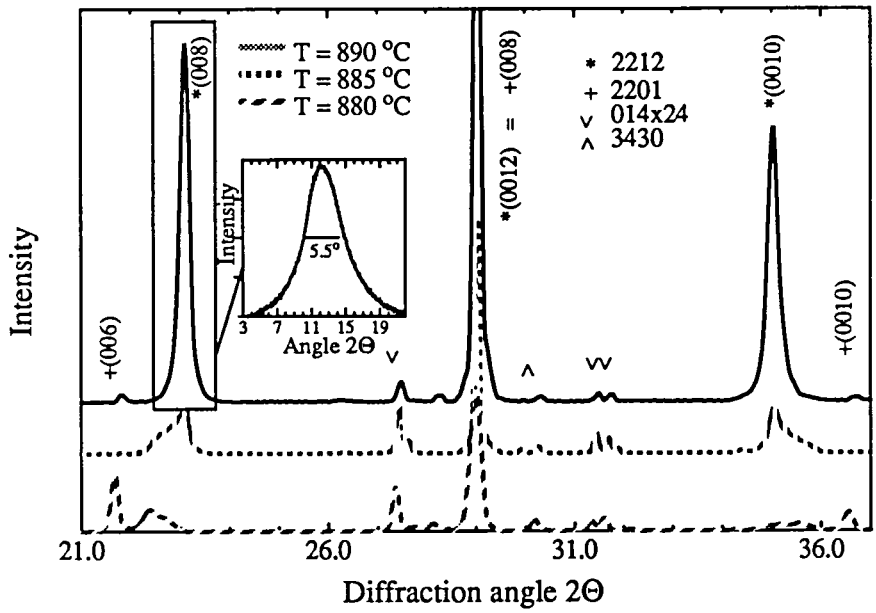

Fig.2 XRD patterns of Bi-2212 thick films with diffrent maximum processing temperatures. The inset shows a rocking curve of the (008)-reflection of the Bi-2212 phase.

Influence of annealing

The Cu-free and the Bi-free phases are the solid phases of the peritectic melting. On cooling, they react with the liquid to form Bi-2201 or Bi-2212. In contrast to bulk material, where the 2201 phase forms first and is transformed to the 2212 phase during annealing at 850 °C in O_2 by liquid/solid and solid/solid reactions [9], the Bi-2212 phase in thick films is the primary phase, formed by controlling the maximum processing tem-

perature in the narrow temperature range of 3 - 8 °C above the solidus temperature. Partial melting above this temperature leads to large amounts of secondary phases which cannot be dissolved by annealing. The transformation from Bi-2201 to Bi-2212 remains incomplete and the amount of the Bi-free and Cu-free phases is hardly decreased. The different behavior of bulk and thick films is attributed to the different lengths of the oxygen diffusion paths. In bulk the remaining oxygen deficiency after partial melting controls the phase formation, whereas in thick films the oxygen uptake is much faster. Therefore, the cations influence the phase formation, leading to the direct crystallization of Bi-2212, if the volume fraction of the 3430-phase remains small.

b) Properties

The superconducting properties (T_c, T_{irr}, j_c) are strongly influenced by the processing parameters. An optimized heat treatment schedule leads to a critical temperature T_c = 92K, an irreversibility temperature T_{irr} = 88K, a critical current density j_c = 18000 A/cm^2 at 77K/0T and j_c = 350000 A/cm^2 at 10K/0T (1μV/cm-criterion) in 20 μm thick films. Critical transport currents up to 30A (corresponding to j_c = 15'000 A/cm^2) were measured resistively in samples of 1cm x 2cm x 20μm size. Fig. 3 illustrates that applied magnetic fields strongly decrease the critical current density depending on the orientation of the external fields. Only the component perpendicular to the (a,b)-plane of the 2212-grains decreases j_c. The I-V characteristics of the thick films obey a power law $V \sim I^{\alpha}$ (fig.4) with a smaller exponent α than found in bulk material at 77K [11]. The α measured at 77K is dependent on the external field. This confirms other results going more into the theory [12].

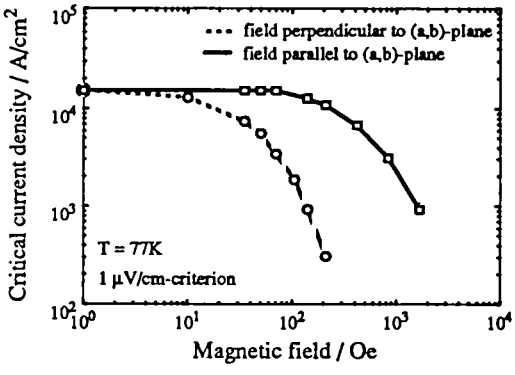

Fig.3 Critical current densities for applied magnetic fields at 77K.

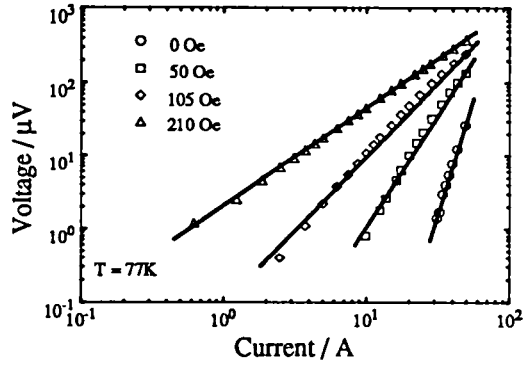

Fig. 4 I-V characteristics for Bi-2212 thick films. at 77K.

Influence of maximum processing temperature

In fig. 5 the critical current densities determined at 77K/0T are shown as a function of the maximum temperature. Maximum j_c are obtained only in the narrow range of 876 ± 3 °C as maximum temperature. The inset of fig.5 shows that different maximum temperatures

shift the j_c-T curve parallel to higher or lower values without a remarkable change in the shape of the curves. This indicates that j_c is controlled by the same parameter over the whole temperature range from 10 to 77K. We therefore suggest that this behavior can be attributed to the connectivity of the current leading paths, rather than to pinning or granularity.

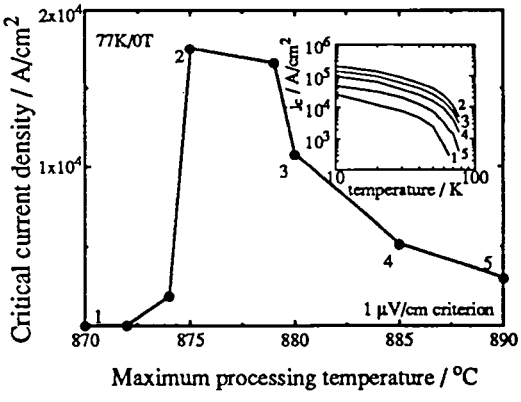

Fig.5 Critical current densities for different maximum processing temperatures at 77K. The inset shows the critical current densities from 10 to 85K.

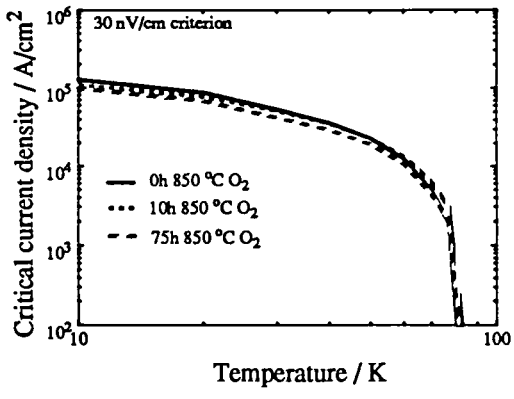

Fig.6 Critical current densities for different annealing time periods at 77K.

Influence of annealing

Samples processed at 876 °C were annealed at 850 °C in O_2 for different time periods. The critical current densities were equal over the whole temperature range from 10 to 85K for annealing 0, 10 and 75 hours (fig.6). Thus, annealing in the single-phase region at 850 °C in O_2 does not increase further the critical current density if the sample was partially molten within the optimum processing window.

In addition, samples with different maximum processing temperatures were measured before and after annealing for 50 hours (inset of fig. 5). The critical current densities did not change at all. Thus, annealing in the single-phase region at 850 °C in O_2 does not compensate the loss of critical current density caused by partial melting outside of the optimum processing temperature range. These observations are in good agreement with the analysis of the microstructures showing that the volume fraction of the secondary phases was not reduced by annealing.

Influence of processing atmosphere

Fig.7 shows that the shape of the j_c-T curve of samples processed in air is different from those processed in O_2. At low temperatures the critical current densities are the same but at higher temperatures the values for air-processed samples are lower. The microstructures of the samples have to be analysed more carefully to see wether different microstructures cause this different behavior for higher temperatures. So far, XRD-patterns show less 2201-intergrowths in 2212-grains in air-processed samples.

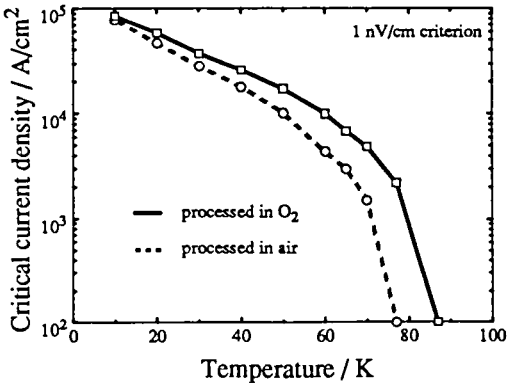

Fig.7 Critical current density for samples processed in air and O_2 from 10 to 85K.

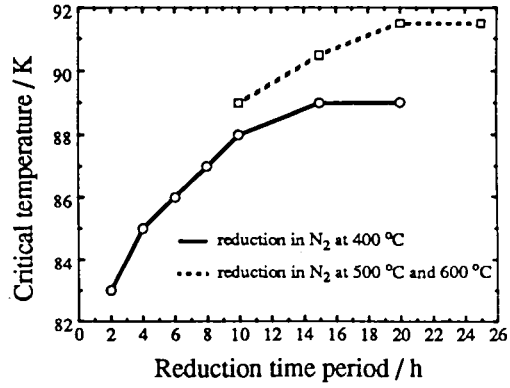

Fig.8 Critical temperature for different reduction time periods and temperatures.

Influence of reduction treatment

Reducing the samples at temperatures below 600 °C in N_2 adjusts the oxygen content without affecting the microstructure. It shifts the critical temperature T_c and the irreversibility temperature T_{irr} to higher values and thus increases j_c at 77K. Fig. 8 shows that annealing for 20 hours at temperatures between 500 and 600 °C optimizes T_c, T_{irr} and j_c at 77K.

Summary

Highly aligned Bi-2212 thick films were prepared by tape casting and partial melting on Ag-substrates. The maximum heat treatment temperature was found to be the most important processing parameter for microstructure and properties. It has to be controlled within 5 to 10 °C above the onset of the peritectic melting to minimize the amount of secondary phases and to maximize the critical current density at 4 and 77K. Annealing at 850 °C in O_2 did not change the critical current densities at all and the volume fraction of the secondary phases was not significantly reduced.
Thus the amount of the secondary phases is strongly correlated to the critical current density. Additionally, the connectivity of the current leading paths is the limiting factor over the whole temperature range rather than pinning or granularity.

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