**Melt-Texturing of Carbon Containing $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$:
Influence of Processing Parameters on Microstructure and Flux-Pinning Behavior***

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Abstract

A detailed study of the flux-pinning behavior of sintered and melt-textured $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ has been carried out by means of microstructural investigations (optical microscopy, SEM, TEM, EDS, DTA, and XRD) and magnetization measurements. It was found that both microstructure and magnetization behavior strongly depend on the starting material, the production method, and the maximum processing temperature. In our experiments, the critical current density, J_c , increased with increasing processing temperature between 920 °C and 1050 °C ($25 - 130 \text{ emu/cm}^3$), but those samples processed at temperatures just above the peritectic transformation point (1020 °C and 1030 °C) exhibited a decreased J_c . The carbon content of the starting powder and the powder's melting behavior seem to play an important role in the development of microstructure and flux-pinning behavior during melt-texturing.

A comparison of our data with previously published results shows that an optimized melt-texturing process can result in materials with critical current densities comparable to those of samples produced by Quench-Melt Growth.

I. Introduction

Bulk samples of the ceramic superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (123) are generally produced either by solid-state sintering below the peritectic melting of 123 or by solidification from the partial melt during slow cooling through the peritectic transformation point at about 1015 °C.

Sintered samples always show weak link behavior at the grain boundaries, limiting the critical current density in these samples to less than 1000 A/cm² at zero field and showing a drastic decrease of J_c in the presence of magnetic field (1).

With the invention of the melt-texturing process (2,3) it became possible to produce larger bulk samples with minimized weak-link regions, and therefore much higher critical current densities were obtained. Recently, domains with sizes up to several inches have been grown (4). In these bulk materials, however, the critical current density is still limited by the flux-pinning strength, which needs to be optimized particularly for largescale applications such as magnetic bearings. Several processing methods, such as Quench-Melt Growth (5), Melt-Powder-Melt-Growth (6,7), Powder-Melt-Process (8), and Solid-Liquid-Melt-Growth (9,10) have been developed to improve the current-carrying capacities of $\text{YBa}_2\text{Cu}_3\text{O}_x$ (123) by introducing defects into the microstructure of the bulk materials. Many defects have been considered as strong flux-pinning centers, including small precipitates (9-15), phase boundaries (16,17), stacking faults (18-20), dislocations (15,18,19), twin boundaries (15,18,21-23), and point defects such as oxygen or cation disorder (18-20,24). While researchers agree that all defects will have some impact, it has been controversial what type of pinning mechanism is responsible for the enhanced critical current densities achieved by these methods.

In general, it is believed that an increasing critical current density can be associated with a decreasing size and an increasing number density of the

precipitates, normally $\text{Y}_2\text{BaCuO}_5(211)$, in the microstructure (assuming a homogeneous distribution and constant volume fraction). The small size of the 211 particles produced by Quench-melt-growth (QMG) and Melt-Powder-Melt-Growth (MPMG) methods ($< 1 \mu\text{m}$) compared with the size of particles produced by the Melt-Textured-Growth materials (10 - 40 μm) was found to be a result of platinum contamination due to crucible reactions (25). Extremely fine precipitates ($< 0.1 \mu\text{m}$) have recently been found in Solid-Liquid-Melt-Growth (SLMG) samples (10) as well as in normally melt-textured samples (11), without platinum doping.

To achieve high flux-pinning, one must prepare a microstructure with a homogeneous distribution of pinning defects with a separation that matches the flux-line lattice spacing. The spacing of the flux-line lattice is about 50 nm at a magnetic field of 1 T and changes with the applied field. Therefore, a material with good flux-pinning properties should have a defect structure in this order of magnitude.

Carbon can be introduced into $\text{YBa}_2\text{Cu}_3\text{O}_x$ in different ways. During powder calcination it can be introduced in the form of carbonates of the precursor materials. During handling and processing in air, CO_2 can be absorbed into the material from the surrounding atmosphere (26,27). In special processing techniques, such as tape casting or wire extrusion, carbon is introduced in the form of the organic binders and other reagents (28). Commercially available powders often contain a few tenths of a weight-percent of carbon. The presence of small amounts of CO_2 in the sintering atmosphere has been reported to result in the formation of tetragonal 123 at grain boundaries as well as the formation of barium cuprates. At higher concentrations of CO_2 , a complete decomposition of 123 results, with formation of phases such as barium cuprates, 211, and $\text{Y}_2\text{Cu}_2\text{O}_5$ and (29-31).

In this paper we focus on the development of the microstructure and magnetization behavior in bulk $\text{YBa}_2\text{Cu}_3\text{O}_x$ produced from commercially available

123 powders. In a series of experiments, the processing parameters such as the maximum processing temperature (920 °C - 1080 °C), the processing technique (sintering, melt-processing), and the starting material have been varied to obtain microstructural changes. We have determined that the magnetization behavior is strongly affected by these parameters. For samples processed below 1000 °C (sintering), a consistent increase in the intragrain J_c with increasing processing temperature was found. The largest J_c was achieved by melt-texturing at about 1040 °C - 1050 °C. The magnetization of these melt-textured samples is comparable with that of samples prepared by the QMG process (14). This magnetization behavior can be related to the structural changes in the material.

II. Experimental Method

Two starting powders were used for this study. Both powders were purchased from commercial vendors and then examined in the laboratory. Chemical analyses revealed that the two starting powders had only minor differences in chemical composition Table 1, specifically, the carbon content of powder I was slightly higher than that of powder II. X-ray diffraction revealed traces of $BaCuO_2$ and 211 in powder I. DTA-curves of both powders revealed a minor reaction peak about 100 °C below the peritectic reaction, indicating that both materials contained small amounts of secondary phases.

The average grain size of both powders was measured with a MICROTRAC particle size analyser. Powder I (~1.7 μm) was smaller than powder II (~5.8 μm), leading to a better densification during sintering and, probably, to a faster melting of this powder.

Two series of experiments were conducted. The first series consisted of five samples sintered at maximum temperatures of 920 °C, 940 °C, 960 °C, 980 °C, and

1000 °C for 24 h. The second series consisted of six samples processed by melt-texturing, with maximum processing temperatures of 1010 °C, 1020 °C, 1030 °C, 1040 °C, 1050 °C and 1080 °C. These six samples were cooled from these maximum temperatures to 980 °C at a rate of 1 °C/h. Powder I was used for both series of experiments. Both series of experiments used three 2-g pellets of powder I, pressed at about 3600 kg/cm². The heat treatment was carried out in alumina crucibles in air. In order to minimize the influence of possible crucible reactions, only the upper parts of the samples were used for the microstructural investigations and the magnetization measurements.

The initial heating rate and the subsequent cooling rates were the same for both series of experiments. Heating rates were 200 °C/h from room temperature to process temperature; cooling rates were 10 °C/h between 980 °C and 800 °C and 100 °C/h between 800 °C and room temperature. The temperature was measured with the W/Re-thermocouples placed close to the crucibles' wall.

Powder II was used for additional melt-texturing experiments at 1040 °C and 1050 °C to investigate its influence on the development of the microstructure and the flux-pinning behavior during melt-texturing. All these experiments were carried out under the same processing conditions as described above.

After processing parts of the samples were characterized with optical microscopy, scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDS). These samples were diamond polished and handled in flowing oxygen to avoid surface reactions.

Other samples were characterised by transmission electron microscopy (TEM), DTA, XRD, and magnetization measurements. These samples were cooled in liquid nitrogen to minimize the formation of dislocations and other crystallographic defects. The samples were then crushed in an agate mortar and oxygenated for 48 h at 450 °C in flowing oxygen atmosphere. All samples showed a similar particle size and particle distribution. DTA characterization was carried out with 300 mg powder

in a flowing oxygen atmosphere; heating and cooling rate was 10 °C/min. The magnetization measurements were performed in a vibrating sample magnetometer. Crushed powders (100 mg) were used in the magnetization measurements because they offer several advantages. First, by grinding the material to an average particle size well below the grain diameters in the bulk materials, one can establish a more accurate definition of the loop size. Weaklink regions such as grain boundaries and microcracks will break more easily as homogeneous bulk materials. Thus the influence of the grain boundaries and the microcracks on the loop size should be reduced. Second, by using small particles with similar size distribution, one can compare materials produced by different technologies, such as sintering or melt-processing. Furthermore, the demagnetization effects will be similar in all the samples used for the magnetization measurements. Third, by randomly orienting the particles in the magnetic field, one can reduce the effect of the magnetic anisotropy on the critical current density.

The apparent critical current density, J_c , was estimated using Beans Model (32,33):

$$J_c = 30 \Delta M / d. \quad (1)$$

Here ΔM is the width of the magnetization loop at a certain temperature and applied field, and d is the size of the current loop, normally the average grain size for sintered materials or the sample size for single crystals or melt-textured materials.

The magnetic field was applied by a superconducting magnet in a gas-flow type cryostat at a rate of 0.8 mT/s. Temperature from 4.2 K to 70 K was monitored with a carbon glass thermometer. Above 70 K, a platinum resistance thermometer was used to control the temperature.

III. Results and Discussion

After the two series of experiments processed with powder I, three different microstructures were found by optical and scanning electron microscopy. Samples processed with maximum processing temperatures between 920 °C and 1010 °C showed typical sintered microstructures with open and closed porosity (Fig. 1). Magnetization measurements performed at 4.2 K showed continuously increasing ΔM at 1 T from $\sim 30 \text{ emu/cm}^3$ at 920 °C to $\sim 90 \text{ emu/cm}^3$ at 1000 °C and 1010 °C (Fig. 2).

Samples processed at maximum temperatures of 1020 °C and 1030 °C showed high amounts of secondary phases in otherwise very different microstructures. The microstructure of the 1020 °C sample was similar to the sintered samples, while the microstructure of the 1030 °C sample looked more like the melt-textured samples. XRD and DTA (Fig 3) confirmed the existence of a high amount of secondary phases in these samples, whereas only minor amounts of secondary phases could be found in the samples sintered at lower temperatures or melt-textured at higher temperatures. The samples in this transition region showed only small magnetization hysteresis (Fig. 2).

Samples processed at maximum temperatures of 1040 °C and 1050 °C showed melt-textured structures with only minor amounts of secondary phases but with a large number of big cavities inside the pellets (Fig. 4). No cavities were found close to the surface of the material. For these samples very high ΔM values, well above 130 emu/cm^3 (4.2 K, 1 Tesla), were observed (Fig. 2).

Magnetic measurements performed at higher temperatures (50 K, 77 K) showed the same correlation between ΔM and the processing temperature (Fig. 2, insert).

At higher temperatures (50 K, 77 K) the melt-textured samples exhibit a fish-tail behavior within the measured field range (Fig. 5), whereas no such behavior could be detected for the sintered materials. Since the particle size, temperature, and oxygenation time were kept constant for all samples, oxygenation treatment is not likely to have affected the magnetization measurements.

The sample processed at a maximum temperature of 1080 °C segregated strongly during processing and hence will not be discussed in detail.

Figure 6 shows three magnetization curves, two of the melt-textured-growth (MTG) samples and one of a quench-melt-growth (QMG) sample. The two MTG samples were processed in the same way but with the different starting powders. The QMG sample was processed by the method developed by Murakami et al. (13). While the QMG-sample and the MTG-sample produced with powder I show a large hysteresis loop, the second MTG-sample (powder II) exhibits only a very small hysteresis loop. Two conclusions can be drawn from this comparison:

1. The flux-pinning behavior of a melt-textured material is strongly dependent on the starting material
2. It is possible to produce a material with an intragrain critical current density comparable to that of QMG-samples by conventional melt-texturing.

To find the reason for the different behavior of the two melt-textured samples, we carried out TEM investigations. In both samples large numbers of twin boundaries, stacking faults, and dislocations were found. Additionally, the sample made from powder I revealed a large number of fine precipitates, visible at higher magnifications. Electron diffraction patterns taken from these regions show a combination of spot and ring pattern (Fig. 7). The spot pattern belongs to 123, while the rings show a good match with BaCuO₂. It is therefore possible that this region consists mostly of YBa₂Cu₃O_x with a large number of fine (~10 nm) BaCuO₂-precipitates. Ullrich et al. (11) have reported BaCuO₂-precipitates in melt-textured

materials produced in a similar way as described in this paper. They found an average precipitation size of 35 nm and a density of about $6 \times 10^{19} \text{ m}^{-3}$. They also reported a large hysteresis loop and fish-tail behavior for their sample. Because of the large differences between the magnetization loops of the two melt-textured samples and because the existence of the fine BaCuO_2 -precipitates is the only visible difference between both samples, we assume that these precipitates are responsible for the good material properties of the melt-textured material processed from powder I.

As reported earlier, the only two differences between the two starting powders were the slightly higher total carbon content and finer particle size of powder I. After processing, however, a major difference was detected between the two melt-textured materials; no large voids were formed in the material processed from starting powder II, whereas large voids were found in the inner core of the material processed from powder I. Thermogravimetric analyses showed, after an initial slight increase of weight, a weight loss between 500 °C and 800 °C. This weight loss was in good agreement with the expected oxygen loss. At higher temperatures, an increasing weight loss was observed. At these elevated temperatures the release of CO_2 from both powders was detected. We assume that, because of the differences in the particle size, some CO_2 was trapped inside the pellet made from powder I, possibly a result of the fast sintering and melting of the fine particles. The coarser particles of powder II on the other hand, probably sintered and melted more slowly, giving the CO_2 more time to leave the sample. Thus large voids formed in the inner core of the samples processed from powder I, whereas a very dense structure without voids was formed in the sample prepared from powder II. A void free structure could only be formed with powder I if the powder was pre annealed for several hours at elevated temperatures to reduce the carbon content before the pellets were pressed. Our results are in good agreement with experiments of Shaw et

al. (29), who found that at 975 °C the formation of closed or open porosity in a sintered material strongly depends on the particle size of the starting material. In ac susceptibility measurements, Shaw et al. also found a stepped superconducting-normal transition for closed-porosity material sintered at 975 °C and speculated that this behavior originates from carbon incorporations into the 123-structure. Other authors (30, 31) investigated the influence of CO₂-containing atmospheres on the phase development of sintered 123 and found that secondary phases such as CO₂-containing BaCuO₂ and BaCu₂O₂ can be formed during the heat treatment. Also reported was the fact that thin layers of tetragonal 123 at the grain boundaries could not be transformed to orthorhombic 123 by oxygenation treatments due to the influence of carbon. Following these results and taking our own measurements into consideration, we conclude that the fine BaCuO₂ precipitates are most likely caused by the incomplete reaction during the resolidification of 123 as a result of dissolved carbon in the melt.

We note that our conclusion is based on the assumption that the good flux-pinning behavior is not affected by small regions of tetragonal 123 or by other defects within the structure. Nevertheless, Ullrich et al. (11) found in their sample oxygen-deficient regions near the grain boundaries. These regions might have been a result of carbon contaminations as reported by Gao et al. (30).

A possible explanation for the fish-tail behavior, which was found at higher magnetic fields for the materials melt-textured at 1040 °C and 1050 °C (powder I), can be found by taking into consideration a broadened superconductor-normal transition observed by Shaw et al. (29). They found a step-like transition with T_c at about 55 K for a powdered carbon-containing sample that was reoxygenated at 500 °C for 20 h. Areas with a lower transition temperature can become normal in presence of magnetic fields, increasing their flux-pinning strength and thus resulting in a fish-tail behavior, as suggested by Daeumling et al. (24).

IV. Conclusions

Commercially available carbon-containing $\text{YBa}_2\text{Cu}_3\text{O}_x$ powders were sintered and melt-textured at maximum processing temperatures between 920 °C and 1050 °C. An increasing intragrain critical current density was found with increasing processing temperature, with the exception of the samples processed at 1020 °C and 1030 °C. The melt-textured samples (T_{max} : 1040 °C, 1050 °C) showed a critical current density comparable to that of samples made by the QMG process. A possible reason for the good flux-pinning behavior is the formation of BaCuO_2 precipitates in the 123 matrix because of the presence of carbon trapped within the sample as a result of the high viscosity of the melt at the processing temperatures. The melting behavior or the grain size respectively of the starting powder has a strong influence on the amount of carbon trapped in the sample and therefore on the final microstructure and the flux-pinning behavior.

A number of questions are still open and need further investigation. How is the carbon distributed in the starting material and in the final microstructure? What mechanism results in the increasing critical current density with increasing processing temperature for the sintered samples and what exactly is the reason for the high amount of secondary phases in the 1020 °C and the 1030 °C samples, leading to the weak magnetization values? Can there be possibly other microstructural defects, such as fine inclusions of tetragonal 123 or other defects? Is it possible to achieve this microstructure and these magnetization values by controlling the atmosphere during the melt-texturing process?

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Table caption:

Tab 1: Chemical composition of the two starting powders used for all experiments. Melt-texturing with powder I resulted in samples with high critical current densities, while powder II produces low critical current densities.

Figure captions:

Fig. 1: Typical sintered microstructure of a pellet sintered at 1000 °C for 24 h. Small grains on the order of 10 to 50 nm are sintered to a porous structure.

Fig. 2: Magnetization/critical current density as a function of the processing temperature for different applied fields and different temperatures. Measurements are taken from powdered samples with random domain orientation. Solid lines are guidelines for the eye only. In general, an increasing critical current density can be found for an increasing processing temperature. For processing temperatures directly above the peritectic melting point of 123, a drastic decrease of the critical current density can be observed. Critical current densities are calculated with Bean's formula with an average current loop size d of 15 mm. The critical current density of the 1050 °C sample is about five times higher than that of the 920 °C-sample at all applied fields.

Fig. 3: Melting behavior of three samples processed with different maximum processing temperatures. The sample processed at 1030 °C shows a melting behavior that is controlled by the large amount of secondary phases present in this sample, while the samples processed at 1000 °C and at 1050 °C show no melting or only a minor amount of melting from secondary phases.

Fig. 4: Microstructure of a sample melt-textured at 1040 °C. Within the 123 domains large 211 precipitates are visible. The core of the pellet shows a number of large pores that were introduced into the pellet during processing and that resulted in a significant deformation of the whole pellet. The outer shell of the pellet is free of the large pores, leading to the assumption that CO₂ released during processing and trapped in the viscous melt led to the pore formation in the core of the pellet, while the gas was able to leave the shell of the molten sample fast enough to avoid the formation of bubbles.

Fig. 5: Magnetization curves at 77 K for two samples processed at maximum temperatures of 1000 °C and 1050 °C. The sample processed at 1050 °C shows a fish-tail behavior, while no fish-tail behavior can be observed in the other sample. The fish-tail feature gives the 1050 °C sample a good critical current density between about 0.5 and 2.5 Tesla. Above this value the magnetization curve collapses for both materials.

Fig. 6: Magnetization curves of three samples melt-grown samples at 4.2 K for fields up to 5 Tesla. The QMG-sample was prepared by the method of Murakami et al. (see (13) for details) with an additional 6 % 211. The two MTG-samples were processed in the same way, with maximum processing temperatures of 1040 °C, but from different starting powders. While the QMG sample and the MTG I sample showed equally good magnetization behavior, MTG II exhibited only a weak magnetization curve.

Fig. 7: TEM picture of a sample prepared at a maximum temperature of 1050 °C from powder I. A very large number of fine (~10 nm) precipitates can be seen. Electron diffraction showed that the main crystal is 123 (spot pattern) with a large number of fine BaCuO₂ precipitates (ring pattern) included in the bulk material.

	Powder I	Powder II
Cation	%weight	%weight
Ag	< 0.006	< 0.006
Al	< 0.010	< 0.010
B	< 0.005	< 0.005
Ba ^a	41.4	41.3
Be	< 0.001	< 0.001
Ca	< 0.001	< 0.001
Cd	< 0.001	< 0.001
Co	< 0.005	< 0.005
Cr	< 0.001	0.006
Cu ^a	29.4	29.4
Fe	< 0.005	0.008
Mg	< 0.001	< 0.001
Mn	< 0.001	< 0.001
Mo	< 0.005	< 0.005
Ni	< 0.005	< 0.005
Pb	< 0.005	< 0.005
Pt	< 0.005	< 0.005
Sn	< 0.010	< 0.010
Sr	0.006	0.001
Ti	< 0.002	< 0.002
V	< 0.001	< 0.001
Y ^a	14.15	14.22
Zn	< 0.005	< 0.005
Zr	< 0.003	< 0.003

^a: +/- 3 %, all others +/- 20 %

Leachable Anion	µg/g	µg/g
NO ₃ ⁻	57	47
Total Carbon	%weight	%weight
C	0.158	0.136

Tab. 1

Fig 1

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7