Microstructural investigations of melt grown YBa$_2$Cu$_3$O$_7$

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Abstract. The results of microstructural investigations on bulk YBa$_2$Cu$_3$O$_7$ prepared by melt growth process are reported.

Keywords. Melt growth; high temperature superconductors; microstructure; current density.

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1. Introduction

Bulk sintered high $T_c$ superconductors have low values of critical current densities ($J_c$) due to the presence of secondary phases at grain boundaries, poor connectivity between the grains and lack of texture in the materials. Several fabrication techniques such as magnetic field alignment (Chen et al 1989), sinter forging (Robinson et al 1987), and melt textured growth (Jin et al 1988; Murakami et al 1989; Salama et al 1989) had been reported to enhance $J_c$ values. Except for the melt growth processes, other methods produced only insignificant improvements in $J_c$. The high critical current densities in melt processed YBa$_2$Cu$_3$O$_7$ are due to aligned microstructures, improved coupling between the grains and also the introduction of non-superconducting inclusions such as Y$_2$BaCuO$_5$ (Matsushita et al 1989). The inclusions contribute to improved flux pinning in the materials.

We report in this paper, investigations on melt grown YBa$_2$Cu$_3$O$_7$, (123). The samples are characterized by optical microscopy and transmission electron microscopy (TEM).

2. Experimental

YBa$_2$Cu$_3$O$_7$ was prepared by dissolving appropriate amounts Y$_2$O$_3$, BaCO$_3$ and Cu metal in nitric acid and evaporating the solution. The nitrate precursors thus obtained were decomposed at 400°C and the resulting powders were presintered at 900°C. Pellets were made from the presintered powders and annealed at 950°C for 16 h. One of the pellets was processed by conventional sintering method at 950°C and cooled to room temperature in oxygen atmosphere. Remaining pellets (dia = 20 mm) were processed by melt growth technique. In this process, the samples were rapidly heated to 1100°C and then cooled slowly from 1020°C to 970°C at a rate of 1°C per hour through the peritectic formation temperature of YBa$_2$Cu$_3$O$_7$. The slow cooling
was done in an atmosphere of flowing oxygen. The samples were further oxygenated while slowly cooling (10°C/h) from 600°C to 400°C. They were then furnace cooled to room temperature. The specimens for TEM observations were prepared by ion beam milling of 3 mm disks.

3. Results and discussion

Figures 1 and 2 show TEM micrographs from conventionally processed YBa$_2$Cu$_3$O$_7$. A molten globule CuO (as identified by EDX) can be seen in figure 1. Under higher magnification, the CuO melt was seen to form a thin layer between the adjacent grains to a thickness of a few hundred Å. In addition, molten BaCuO$_2$ also forms thin layers between the grains as shown in figure 2. Apart from the lack of texture in the material, these impurity molten phases act as a serious impediment to achieving high current densities in conventionally processed 123.

The microstructure of melt processed 123 is entirely different as revealed in figure 3. The optical micrograph shows that the grains of 123 are aligned parallel to one another. They are a few millimeters in length and $\sim 15\mu$m in width. In figure 4 an optical micrograph obtained under polarized light is shown. Twin boundaries can be seen cutting across the grains of 123. Some of the grain boundaries reveal the presence of microcracking, the crack width being of the order of $2\mu$m.

Murakami et al (1990a) have made similar observations on melt grown samples and found grain boundary cracks produced due to the transformation of the high

![Figure 1. TEM micrograph from conventionally processed 123 showing a molten globule of CuO at the grain boundary. A thin layer was found to spread from this molten globule to the space in between the grains contributing to lower current carrying capacities.](image)
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Figure 2. A TEM micrograph showing molten \( \text{BaCuO}_2 \) layer at the grain boundary in conventionally processed 123.

Figure 3. Grain alignment in melt grown 123 is revealed by an optical micrograph.

temperature tetragonal phase to the low temperature orthorhombic superconducting phase. They have shown that the addition of silver can prevent the formation of such cracks (Murakami et al 1990b). We have observed that the cracks can contribute to a deterioration of the material by interaction with the environment and the formation of \( \text{BaCO}_3 \) at the cracked grain boundaries. A TEM micrograph in figure 5 reveals the presence of \( \text{BaCO}_3 \) at one such boundary in a melt grown specimen. \( \text{BaCO}_3 \) was identified from its electron diffraction pattern. \( \text{CO}_2 \) from the atmosphere can enter through the microcracks in melt grown specimens and cause the formation of such
Figure 4. Optical micrograph obtained with polarized light reveals twin boundaries cutting across several grains of aligned 123.

Figure 5. A TEM micrograph showing the formation of BaCO$_3$ at some grain boundary cracks in melt grown 123 due to interaction with the environment.

layers. An effective method of protecting the material against deterioration and enhancing its fracture toughness would be the addition of silver and work in that direction is in progress.

A few precipitates of the $Y_2BaCuO_5$ phase with a spherical morphology could also be observed within the 123 grains as revealed in the TEM micrograph in figure 6. The presence of $Y_2BaCuO_5$ precipitates can aid flux pinning and enhancement of $J_c$ (Murakami et al 1990a) in melt grown 123. Experiments to optimize the amount and distribution of the precipitates are in progress.

Resistivity measurements on the melt grown sample revealed a zero resistance temperature at 88 K. This is lower than the zero resistance temperature observed in
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conventionally prepared 123 due to the difficulties associated with fully oxygenating the samples.

The critical current densities ($J_c$) of melt grown undoped 123, which is discussed in this paper, were estimated from magnetization measurements (Srinivasan et al to be published). The values showed a wide scatter with $J_s$ ranging from $5 \times 10^2$ to $5 \times 10^3$ A/cm$^2$ at 77 K and at 0.1 T. Though these values show an improvement over those reported in conventionally processed 123 (e.g. Cava et al 1987), they are considerably lower than the best values reported for melt grown samples whose properties have been optimized (Murakami et al 1990a). The low $J_c$ values stem from the low intergrain $J_c$ due to the presence of cracks and also due to the absence of $Y_2BaCuO_5$ precipitates acting as flux pinning centres. Further work aimed at optimizing the properties of the melt grown samples is in progress.

References

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