Enhancement of magnetic pinning in liquid phase sintered YBCO

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Abstract. Liquid phase sintering of YBCO superconductor has been investigated using 900°C- and 950°C-calcined precursors. Magnetic hysteresis, i.e. critical current density ($J_c$), is enhanced at elevated magnetic fields for the samples with the 900°C-calcined precursor of fraction more than 80%. $J_c$ increases steeply as fraction of 900°C-calcined precursor increases from 80% to 100%, which is coincident with anomalous grain growth in the samples. The samples showing $J_c$ enhancement compose of rather rectangular grains with length more than 100 µm, whereas grains of the samples showing no enhancement are rather round and a few tens of µm in diameter. Structural developments with fraction of the precursor and oxygenation behavior suggest that low angle grain boundary pinning is observed in the liquid phase sintered samples.

1. Introduction

Many efforts on YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) processing being under investigation concentrates thin film and melt-growth because of fragile property and week link behavior at grain boundaries of the material. Grain boundaries in a YBCO superconductor are strongly avoided because high angle grain boundaries show weak-link behavior for transport current and cause a flow of magnetic flux quanta, resulting in suppression of critical current density ($J_c$) [1]. On the other hand, a low angle grain boundary was proved to be able to pin magnetic vortexes and act as a pinning center [2]. Diaz et al. showed that a 4-degree grain boundary exhibits $10^6$ A/m$^2$ at 77 K in critical current density, comparable to a bulk superconductor prepared by partial melt growth. Yamada et al. indicated that a low angle grain boundary network may improve critical current density up to $10^{10}$ A/m$^2$ in thin films grown by the liquid phase epitaxy method [3]. Therefore, simple processing to make low angle grain boundary network is very important to investigate.

Sintering process, which typically forms randomly oriented polycrystalline bulks, is one of the simplest methods to form a grain boundary network. Grains of YBCO superconductor in a sintered bulk may couple as weak-link boundaries because of not only being high angle grain boundaries but also being non-superconducting boundary layers formed between the grains, resulting in distinct suppression of $J_c$. In order to remove the non-superconducting boundary layers, liquid phase sintering process has been investigated, because it stabilizes YBCO phase and removes diffuse boundary interface due to thermodynamical phase stability. By adopting liquid phase sintering process, critical current density can be increased at elevated magnetic fields depending on starting precursor and sintering temperature [4]. $J_c$ enhancement has been observed on samples using 900°C-calcined YBCO precursor but no enhancement when using 950°C-calcined precursor. In order to reveal the
role of precursor mechanism in Jc enhancement in liquid phase sintering process, effect of mixture of the two precursors was investigated in this study.

2. Experimental

Two kinds of YBCO precursors were prepared by mixing the raw materials of Y₂O₃, BaCO₃, and CuO in stoichiometry. One is prepared by calcining finally at 900°C and the other at 950°C after a few calcination processes at lower temperatures. Particle sizes of 900°C- and 950°C-precursor were typically 1-2 μm and 5 μm, respectively. Figure 1 shows powder X-ray diffraction patterns of these precursors. In order to reveal the role of precursor in Jc enhancement, mixtures of these two precursors were prepared with fraction of 0, 25, 50, 75 and 100 % (Series-1) and 75, 80, 85, 90, 95 and 100 % of 900°C-precursor (Series-2).

The flux used for the liquid phase sintering was composed of BaO, CuO and BaF₂ with molar ratio of 29:70:1. The melting point of the flux was approximately 920°C in air, forming liquid phase during a sintering process. The flux was added to the mixed precursor by 10% in weight. The precursor-flux mixture was pressed into pellets with approximately 10mm in diameter and 3mm in thickness.

The pellets were sintered for 12 h in flowing oxygen at the beginning temperatures of 920°C. After the samples were sintered, oxygenation was performed at 500°C for 48 h and furnace cooled, which corresponded to the annealing condition of 400°C and quenched to room temperature in the view point of Jc-B behavior. Magnetization was measured by a vibrating sample magnetometer after the oxygenation to obtain magnetic hysteresis loops to estimate critical current density by simple Bean’s model. Magnetic field was applied in a pellet plane. Therefore, rough Jc estimation was carried out using the thickness of the pellets as sample dimension in Bean’s model. After the sintering-measurement procedure, the samples were sintered at a higher temperature to 1005°C (Series-1) and 980°C (Series-2) to investigate sintering temperature dependence. Microstructure was observed by scanning electron microscopy (SEM) after the final sintering process at the highest temperature.

3. Results

Figure 2 shows Jc-B curves of the mixed samples of Series-2 for various fraction of 900°C-precursor, which were sintered at 980°C and measured at 77 K. Samples which have fractions of 900°C-precursor less than 80% show monotonous decrease in Jc-B curve, i.e. no Jc enhancement at fields below 14 kG. On the other hand, samples with 900°C-precursor more than 85% showed a broad peak in Jc and as the fraction of 900°C-precursor increased, value of Jc also increased. Jc’s at the field of 14 kG in the Jc-B curve are plotted in Figure 3. As can be seen in Figure 3, Jc enhancement occurred at fractions exceeding 80% and rapidly increased as fraction increased up to 100%.
Microstructures of samples with 900°C-precursor, which were 75% and 100% in fraction and sintered at 980°C, are shown in Figure 4. 100%-samples consisted of grains whose size is more than 100 µm in length and rather rectangular in shape. On the other hand, samples of fraction less than 75% consisted of a few tens µm in diameter and were rather round. Gradual increase in grain size was observed as fraction of precursor increase from 75% to 100% and shape changed from round to rectangular. It should be noted that $J_c$ enhancement and distinct anomalous grain growth occurred at the same fraction region.

![Figure 2](image1.png)  
**Figure 2** $J_c$-$B$ curves for various fraction of 900°C-precursor (Series 2)

![Figure 3](image2.png)  
**Figure 3** $J_c$ as a function of fraction of 900°C-precursor at the field of 14 kG

![Figure 4](image3.png)  
**Figure 4** SEM photos showing grain size and shape depending on fraction of 900°C-precursor

4. Discussion

Samples whose fraction of 900°C-precursor was more than 80% showed enhanced grain growth than those of fewer fractions. The 900°C-precursor had broader peaks in X-ray diffraction than the 950°C-precursor (Figure 1) and the 950°C-precursor showed enhanced (00l) diffraction than the 900°C-precursor. These indicate that crystalline perfection of 900°C-precursor was poorer. It was obvious that grain size of 900°C-precursor was smaller than that of 950°C-precursor. Generally, poor crystalline perfection and small grain size of starting powder in sintering process, especially liquid phase sintering, can cause extreme anomalous grain growth.

Distinct grain growth occurred in the samples with 900°C-precursor more than 80 %, coincident with $J_c$ enhancement shown in Figures 2, 3 and 4. This indicates that $J_c$ enhancement mechanism strongly correlated with anomalous grain growth. One possible mechanism to explain this correlation is oxygen deficiency [5] in the samples constructed with very large grains, due to low diffusivity of oxygen in the grains. However, experiments on annealing time dependence, even when samples were quenched to room temperature, have indicated that much longer annealing than this experiment would result in negligible difference in $J_c$-$B$ curve [6]. This indicates that oxygen content in the samples is
saturated, meaning that they are in equilibrium with the annealing atmosphere. Therefore, all samples under the same annealing condition should contain the same amount of oxygen. Accordingly, oxygen deficiency is difficult to explain the $J_c$ enhancement of the samples with 900°C-precursor.

Another possible mechanism for understanding the $J_c$ enhancement is related to the structure of the bulks. Diaz et al. investigated magnetic flux pinning at a low angle grain boundary and revealed that magnetic flux can be pinned even at 77 K depending on geometry between magnetic direction and grain boundary [2]. This means that even a randomly oriented polycrystalline bulk can show magnetic flux pinning behavior because some grain boundaries should meet the pinning geometry.

Both samples with 900°C-precursor and 950°C-precursor consisted of randomly oriented grains. What is the reason that 900°C-precursor provides $J_c$ enhancement but not 950°C-precursor? The samples showing no $J_c$ enhancement consisted of small round grains, and therefore, whose surface should be crystallographically rough. Coherence length of oxide superconductor is order of 1 nm and many interface researches revealed that crystallographically rough interface, i.e. “dirt” interface, between grains strongly depress critical current density and pinning property. 900°C-precursor provides large rectangular grains due to growth through liquid phase. Surface of thermodynamically well grown crystal of YBCO is expected to be atomically flat and interface should be “clean” for superconducting coupling. Accordingly, samples consisted of well grown grains show $J_c$ enhancement at elevated magnetic fields.

5. Conclusion
Liquid phase sintered YBCO superconductor was performed using 900°C- and 950°C-precursors. Magnetic hysteresis, i.e. critical current density, was enhanced at magnetic fields higher than 2 kG for the samples for whose fraction of the 900°C-precursor was more than 80% and the enhancement progressed as fraction increased. On the other hand, the samples whose fraction of 900°C-precursor was less than 75% show monotonous decrease of $J_c$ in $J_c$-$B$ diagram and no enhancement up to 14 kG. As fraction of 900°C-precursor increased from 80% to 100% $J_c$ increased steeply. In terms of structural development, distinct anomalous grain growth occurred in the samples of fraction more than 80% and progressed as fraction increase. The samples showing $J_c$ enhancement composed of rather rectangular (probably plate-like) grains with length more than 100 µm, whereas, grains of the samples showing no enhancement were rather round and a few tens of µm in diameter. Oxygenation behavior and coincidence of fractional dependence between $J_c$ enhancement and structural development suggests that low angle grain boundary pinning was observed in the liquid phase sintered samples.

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