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Effects of Y_2BaCuO_5 on the directional growth of $YBa_2Cu_3O_X$ superconductor

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The effects of Y_2BaCuO_5 on the microstructure and superconducting properties of $YBa_2Cu_3O_x$ samples, textured using the directional growth of Y_2BaCuO_5, $BaCuO_2$ and CuO powder mixtures, were studied. Y_2BaCuO_5 moved downward as the sample passed up through the hot zone, and this downward movement affected the superconducting properties of the directionally grown samples. The critical temperature increased, and the resistance transition width decreased as the excess 2 1 1 content in the powder mixture increased up to a value, beyond which the temperature decreased and the width increased. The critical current densities of the directionally grown samples were scattered because of the presence of uncontrollable severe cracks perpendicular to the growth direction. As the hot-zone temperature increased, the critical current density of the directionally grown sample increased up to a maximum value (> 6000 A cm^{-2}) beyond which the critical current density decreased. Compared to data from other studies, the hot-zone temperature required to produce a maximum critical current density was lower.

1. Introduction

Progress towards major applications of the bulk high temperature superconductor has been hindered by low-transport critical current densities (J_c) at the boiling point of liquid nitrogen, and their severe degradation in weak magnetic fields because of the weak link problem in the sintered materials [1]. Several studies [2–4] have succeeded in reducing the weak link problem in bulk samples by employing a melt and directional solidification process which enables the fabrication of well-textured samples with clean boundaries and large grains aligned in a preferred orientation. These samples exhibited dramatically improved transport J_c values at the boiling point of liquid nitrogen of above 10^4 A cm^{-2} in zero magnetic field (H) and of above 10^3 A cm^{-2} at $H = 1$ T as compared to several hundreds and about 1 A cm^{-2}, respectively, for the samples without the texturing.

A technique has been found for preparing 1 2 3 ceramics by reacting Y_2BaCuO_5 (2 1 1), $BaCuO_2$ (0 1 1), and CuO (0 0 1) precursor powder mixture with the following reaction [5]:

$$Y_2BaCuO_5 + 3BaCuO_2 + 2CuO \rightarrow 2YBa_2Cu_3O_6 + 1/2O_2\uparrow \quad (1)$$

This reaction involves two melt forms, one beginning at $\sim 950\,^\circ$C and one at $\sim 980\,^\circ$C, representing 0 1 1 + 0 0 1 → liquid and 2 1 1 + 0 1 1 → 2 0 2 + liquid, respectively. Those melt forms provide a faster reaction than that involving only interatomic diffusion in the solid-state sintering technique. Above $\sim 1015\,^\circ$C, 1 2 3 was found to melt incongruently, forming liquid and 2 1 1 [6].

In previous papers [7, 8], we reported the texturing of bulk 1 2 3 ceramics by directional growth of 1 2 3 grains reacted from 2 1 1, 0 1 1, and 0 0 1 precursor powder mixture, and the effects of pulling speed and hot-zone temperature on the directional growth. The samples consisted of grains several mm long aligned parallel to the growth direction. The microstructure observation and X-ray diffraction (XRD) analysis showed that when the grains have a preferred orientation, the critical current density is improved. The sample grown directionally at 1.5 mm h^{-1} pulling speed and at 1120 °C hot-zone temperature showed a sharp resistivity transition of 91 K zero resistivity and over 6000 A cm^{-2} critical current density. During the previous studies [7, 8], a green section was observed at the end of the directionally grown sample, which may indicate that 2 1 1 moved downward and piled up at the end of the sample as the 2 1 1, 0 1 1 and 0 0 1 powder mixture sample moves up through the high-temperature zone. This downward movement of 2 1 1 may cause yttrium depletion in the directionally grown sample, which may affect the superconducting properties of the sample.

Possible effects of 2 1 1 on the directional growth and the superconducting properties of 1 2 3 samples have been suggested in several studies [4, 9]. Kase *et al.* [9] claimed that 2 1 1 improved the grain

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alignment in the directional growth process. Murakami *et al.* [4] mentioned that 2 1 1 may serve as flux pinning sites and thus improve the critical current density.

In the present paper, we report the microstructure and superconducting properties of textured samples using directional growth of 1 2 3 grains reacted from 2 1 1, 0 1 1 and 0 0 1 precursor powder mixtures having different 2 1 1 contents.

2. Experimental procedure

Y_2BaCuO_5 and $BaCuO_2$ precursor powders were synthesized using solid-state reactions of reagent grade Y_2O_3, $BaCO_3$, and CuO powder mixtures. The processing conditions for the precursor powders have been described in detail in [5]. The mixtures of 2 1 1, 0 1 1 and 0 0 1 precursor powders with different 2 1 1 contents were ground in an automatic agate mortar and pestle for 1 h per each 10 g, and bar samples ($\sim 0.3 \times 0.1 \times 3$ cm) of the powder mixtures with a few drops of organic binder were pressed in a steel mould. After drying in air overnight, the bar samples were carefully heat treated at 850 °C for 1 h to calcine the organic binder and to provide strength for handling. A small hole was drilled at one side of the heat-treated bar sample in order to hang the sample on a constant speed puller using platinum wire. The bar samples were pulled up through a high-temperature zone provided by a small platinum coil inside a kanthal furnace. A schematic diagram and temperature profile of the directional growth furnace have been presented in [8]. The pulling speed in this study was 1.5 mm h^{-1}.

After cooling down to room temperature, both surfaces of the bar sample were ground flat using SiC paper, and the sample was cut in half lengthwise using a diamond saw, one half for superconducting property measurements and the other for microstructural examination. Four electrical contacts on the superconducting property measurement sample were made of silver epoxy. The samples were heat treated to provide better contact between the superconductor and silver epoxy in oxygen flowing atmosphere at 800 °C for 1 h. During cooling down to room temperature, the sample was held at 550 °C for 24 h in order to provide 1 2 3 with appropriate oxygen stoichiometry.

The superconductivity transition temperatures and the critical current densities of the samples were measured using the d.c. four-point probe method. The lead wires carrying the current were attached to the silver contacts using soldering for the critical current density measurements in liquid nitrogen. The voltage drop across the two inner electrical contacts was measured using a Keithley 181 nanovoltmeter, and the temperatures were measured using a Si diode attached to the back side of the sample, and a Lakeshore 805 controller. The microstructures of the textured samples were observed using a polarized microscope.

3. Results and discussion

The samples aligned using directional growth showed a green section at the end of the samples. The green section may indicate that 2 1 1 moved downward as the sample moved up through the high-temperature zone and piled up at the end of the sample. In order to observe the 2 1 1 movement along the directional growth process, pulling was stopped for a sample with stoichiometric 1 2 3 composition in the middle of the directional growth process, and the sample was furnace-cooled to room temperature. Fig. 1 shows a polarized light image of the cross-sectional surface of the sample. The top portion of the sample consists of two long grains (about 5 mm long) aligned parallel to the growth direction. A flat-front boundary was observed at the interface between the directionally grown region and the remaining portion, which indicates that the hot-zone temperature (1120 °C) and the pulling speed (1.5 mm h^{-1}) used in this study were appropriate for the grain alignment. Near 1 mm down from the interface boundary, a lump of green phase (about 2 mm long) was observed in the middle of the sample. It is known that 2 1 1 phase is green in the polarized light beam. This observation indicates that 2 1 1 moved downward as the sample passed up through the hot zone. (This downward movement of 2 1 1 is under investigation and will be described in a subsequent paper.) The 2 1 1 movement may cause yttrium depletion in the sample and affect the superconducting properties of the sample.

In order to investigate the effects of 2 1 1 content on the superconducting properties of 1 2 3, bar samples were directionally grown using the mixtures of 2 1 1, 0 1 1 and 0 0 1 precursor powders having different 2 1 1 contents. Fig. 2 shows temperature against normalized resistance curves of the directionally grown samples having different 2 1 1 contents. The hot-zone temperature and the pulling speed were 1050 °C and 1.5 mm h^{-1}, respectively. The sample fabricated without excess 2 1 1 showed broad resistance transition and zero resistance at about 82 K (the critical temperature). The critical temperature increased, and the resistance transition width decreased as the excess 2 1 1 content increased up to 50 mol % beyond which the temperature decreased and the width increased. Fig. 3 shows temperature against normalized resistance curves of samples with different 2 1 1 contents but sintered at the same condition (1000 °C for 10 h). The sample fabricated with a stoichiometric 1:2:3 powder mixture showed zero resistance at ~ 85 K.

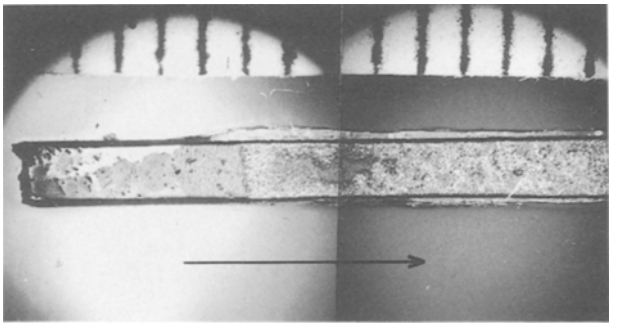

Figure 1 A polarized light image of a sample grown directionally. The directional growth was stopped during the process. Arrow indicates growth direction; space between tick marks = 1 mm.

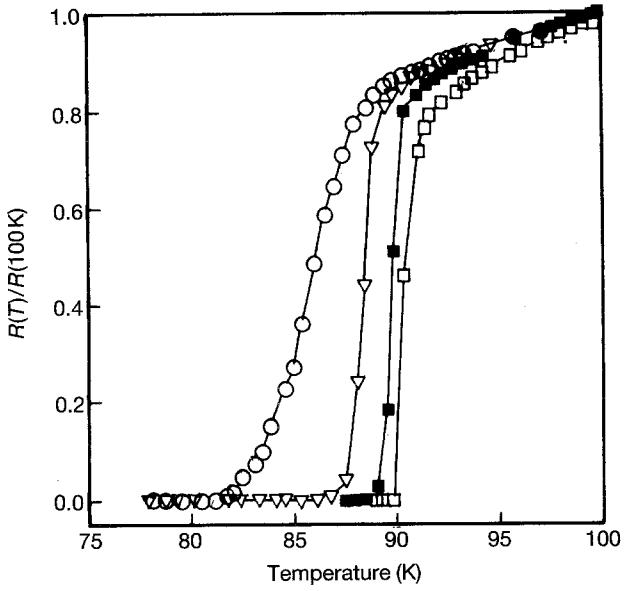

Figure 2 Temperature against resistance curves of samples directionally grown using powder mixtures with different excess 2 1 1 contents. Hot-zone temperature, 1050 °C, pulling speed, 1.5 mm h^{-1}. ○, No excess; ▽, 0.3; □, 0.5; ■, 0.8 mol fraction.

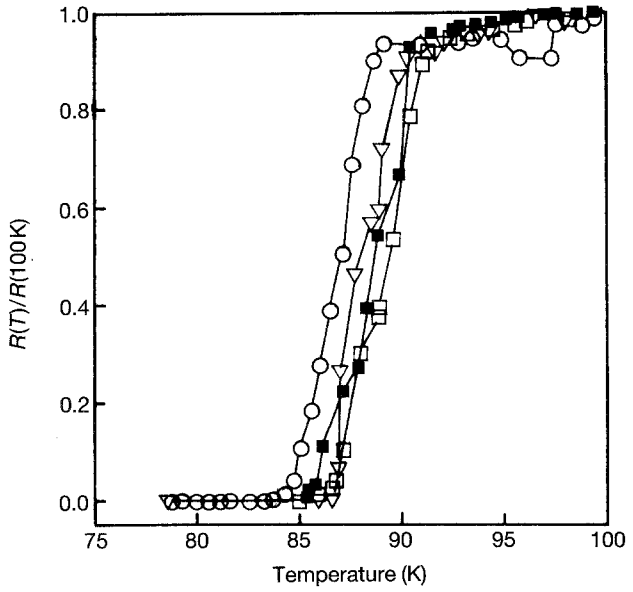

Figure 3 Temperature against resistance curves of samples sintered using powder mixtures with different excess 2 1 1 contents. ○, No excess; ▽, 0.3; □, 0.5; ■, 0.8 mol fraction.

The sample fabricated with the powder mixture having 30 mol% excess 2 1 1 showed a higher critical temperature, and the temperature decreased as the excess 2 1 1 content increased beyond 30 mol %.

Fig. 4 shows relationships between the critical temperature and the excess 2 1 1 content of both sintered and directionally grown 1 2 3 samples. For the samples fabricated with a stoichiometric 1:2:3 powder mixture, the critical temperature of the directionally grown sample is lower than that of the sintered sample, which may indicate that the observed downward movement of 2 1 1 during the directional growth process causes yttrium depletion and affects the superconducting properties of the sample. As the excess

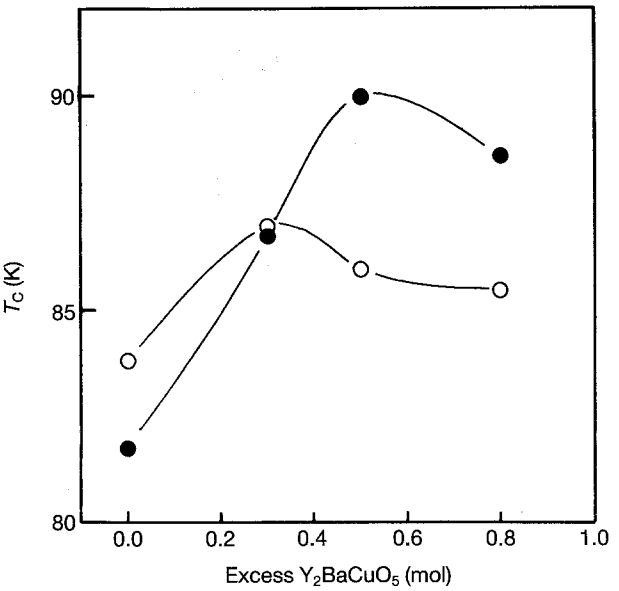

Figure 4 Relationships between excess 2 1 1 content and critical temperature of samples. ○, Sintered; ●, D.S.

2 1 1 content increased, the critical temperature of the directionally grown sample became higher than that of the sintered sample, which may indicate that the excess 2 1 1 in the powder mixture compensated the yttrium depletion. Both samples showed maxima in the relationship. As the excess 2 1 1 content increased up to the maximum, the excess 2 1 1 reacted with impurity phases ($BaCuO_2$, CuO and/or eutectic liquid of $BaCuO_2$ and CuO), the sample consisted of lower impurity content, and the temperature showing zero resistance increased. As the excess 2 1 1 content increased beyond the amount showing the maximum critical temperature, the temperature showing zero resistance decreased; 2 1 1 may also serve as an impurity phase. The excess 2 1 1 content showing the maximum critical temperature for the directionally grown samples was higher than that for the sintering samples, which may indicate that yttrium depletion in the sample due to the 2 1 1 movement in the directional growth process occurs. This observation may indicate that the amount of excess 2 1 1 required in the directionally grown samples was the sum of the amount of 2 1 1 required to give optimum performance in the sintered samples and the amount of 2 1 1 remaining at the end of the bar samples.

Fig. 5 shows the relationship between the 2 1 1 content in the powder mixture and the transport critical current density of the samples directionally grown at 1050 °C hot-zone temperature and 1.5 mm h^{-1} pulling speed. Because some samples (of which the critical current density data are marked with open symbols) showed higher current flowing capability than the limit of the current supply used in this study, and because samples had different current flowing areas, the open circle data are lower than the actual critical current densities of the samples. The data are so scattered that no distinct relationship between the 2 1 1 content and the critical current density was found. A possible source of the data scattering was the current flowing area reduction due

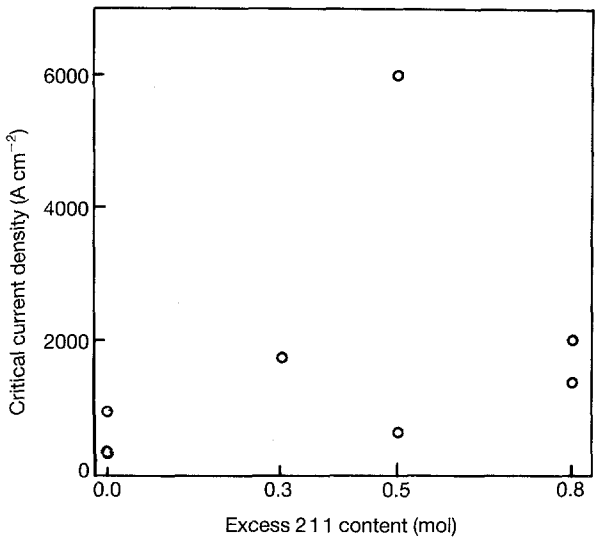

Figure 5 Relationships between excess 2 1 1 content and critical current density of samples directionally grown at 1050 °C hot-zone temperature and 1.5 mm h^{-1} pulling speed.

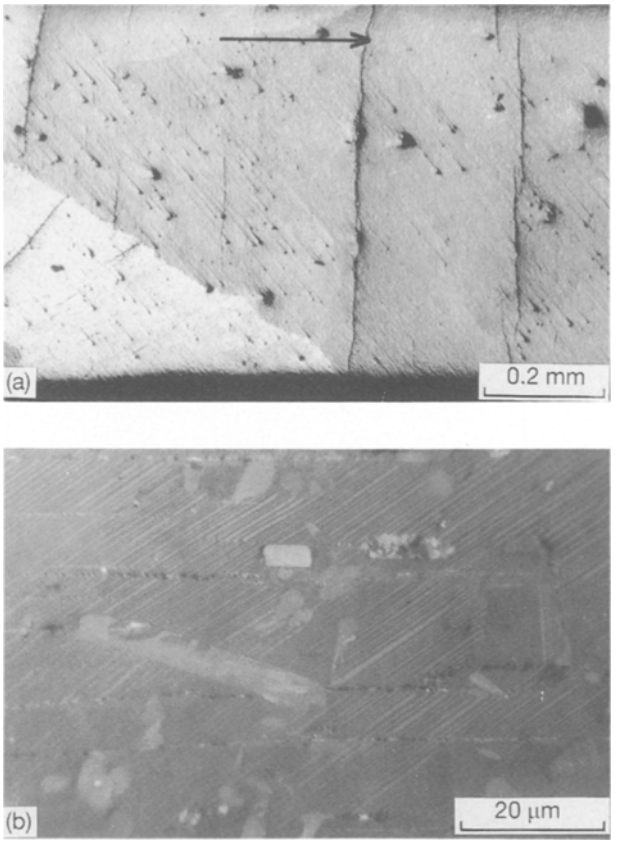

Figure 6 Polarized light images of a sample having severe cracks. Arrow indicates growth direction. (a) Low magnification, scale bar = 0.2 mm; (b) high magnification, scale bar = 20 μm.

to internal cracks in the directionally grown samples. Fig. 6 shows polarized light images of a typical microstructure of a directionally grown sample consisting of severe cracks. Two kinds of crack were observed in the microstructure. The large cracks across almost the whole width of the sample were observed at the low magnification image (Fig. 6a). The sample consisted of several grains (based on the observed contrast in the polarized light image) at the left side of the sample, which passed the hot zone at the early stage of the directional growth process, but consisted of a single grain at the right side of the sample. Different grains showed different crack directions, and the large cracks appear to form at preferred orientation. Because some cracks are perpendicular to the growth direction which is indicated in the figure, and because the current flows parallel to the growth direction, these cracks may significantly decrease the current flowing area and affect the critical current density. This sample showed almost zero critical current density. It was difficult to control the occurrence of the large cracks. Some samples presented large cracks, but other samples did not, even though all samples were directionally grown, cooled and annealed under the same conditions. These uncontrollable cracks may affect the critical current density data and cause the data scattering observed in Fig. 5. The other cracks could be observed in the higher magnification image (Fig. 6b) and are parallel to the growth direction. Because the current flows parallel to the growth direction, the parallel cracks may not significantly affect the critical current density.

Fig. 7 shows a relationship between the hot-zone temperature and the critical current density of the samples grown directionally with the powder mixture having 50 mol % excess 2 1 1. The data on the samples having no excess 2 1 1 [8] and the data of Jin *et al.* [10] are included in Fig. 7 for comparison. As the hot-zone temperature increased, the critical current density increased up to a maximum value beyond which the

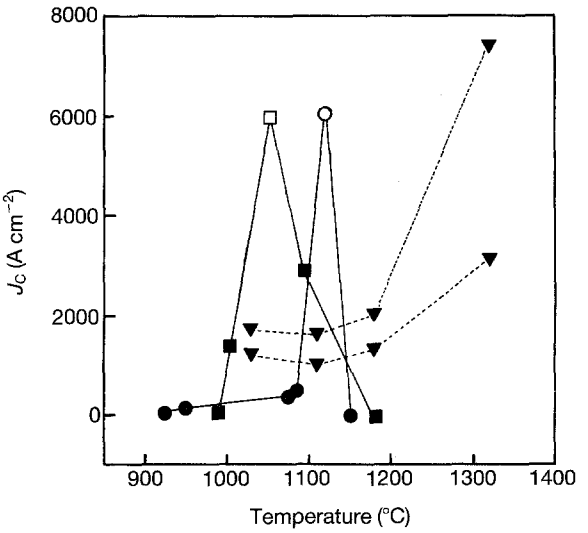

Figure 7 Hot-zone temperature against critical current density data of samples grown at different hot-zone temperatures. Open symbols indicate that data were lower than the actual critical current densities due to the instrumental limitations of this study. Rectangular, circular and triangular points, data from samples with 50 mol % excess 2 1 1, no excess 2 1 1 and data from [10], respectively.

critical current density decreased. For the samples with 50 mol % excess 2 1 1, the hot-zone temperature at which the sample showed a maximum critical current density was 1050 °C, ~ 70 °C and > 200 °C lower than the hot-zone temperatures of the samples having no excess 2 1 1 and Jin's data [10], respectively.

A significant difference between Jin's data and the present studies was the precursor powder used. Jin *et al.* used reacted 1 2 3 powder, but the present study used 2 1 1, 0 1 1 and 0 0 1 powder mixture. The powder mixture used in this study forms liquids at lower temperature, and the liquids may decrease the hot-zone temperature needed for a maximum critical current density.

4. Conclusions

The effects of Y_2BaCuO_5 on the microstructure and superconducting properties of $YBa_2Cu_3O_x$ samples, textured using the directional growth of Y_2BaCuO_5, $BaCuO_2$ and CuO powder mixture, were studied, and the following conclusions were drawn.

1. Y_2BaCuO_5 moved downward as the sample passed up through the hot zone, which may cause yttrium depletion in the sample and affect the superconducting properties of the directionally grown sample.
2. The critical temperature increased, and the resistance transition width decreased for the directionally grown samples as the excess 2 1 1 content in the powder mixture increased up to 50 mol %, beyond which the temperature decreased and the width increased.
3. The critical current density data were scattered among the samples grown directionally under the same conditions, because of the uncontrollable severe cracks perpendicular to the growth direction.
4. As the hot-zone temperature increased, the critical current density of the directionally grown sample increased up to a maximum value beyond which the critical current density decreased. The hot-zone temperature showing the maximum critical current density of the sample with 0.5 mol % excess Y_2BaCuO_5 was lower than that of the sample having a stoichiometric 1:2:3 ratio.

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