Melt-textured growth of polycrystalline $YBa_2Cu_3O_{7-\delta}$ with high transport J_c at 77 K

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The progress toward major applications of $YBa_2Cu_3O_{7-\delta}$-type high-T_c superconductors has been hindered by low critical current densities (J_c) and their significant deterioration in weak magnetic fields. The present work demonstrates that these problems can successfully be overcome through proper microstructural control using molten oxide processing. Melt-textured growth of $YBa_2Cu_3O_{7-\delta}$ from a supercooled melt created an essentially 100% dense structure consisting of locally aligned, long, needle-shaped grains (typically 40–600 μm in length). The needles appear to have their long axes parallel to the conduction plane (basal plane) of the orthorhombic structure, with a low-angle orientation change between adjacent grains. This new microstructure, which completely replaces the previous granular and random structure of the sintered precursor, exhibits a dramatically higher transport J_c (7400 A/cm^2 at 77 K) than the typical sintered materials (J_c = 150–600 A/cm^2). Even more significant is the much reduced field dependence of J_c ($\approx$1000 A/cm^2 at H = 1 T as compared to $\approx$1 A/cm^2 in the sintered structure), indicating that the coupling between grains is much stronger in the new structure. The mechanism responsible for the suppressed weak-link behavior in the melt-textured material is inferred to be the combined effects of the densification, alignment of crystals, and formation of cleaner grain boundaries.

High-temperature superconductivity in copper-oxide-based compounds[1,2] and its potential for important technological applications have led to unprecedented excitement and research in this field.[3-18] For the new superconductors to be useful, they have to be fabricated into desirable shapes, and should carry sufficiently high electrical currents. The difficulty in fabrication of the brittle $YBa_2Cu_3O_{7-\delta}$ ceramic material has been overcome by several different approaches;[6-9] however, the low critical current densities at 77 K in polycrystalline materials and the rapid deterioration of J_c in weak magnetic fields remain a main roadblock to significant technical advancement. Indirect measurements of J_c from the magnetization loops for single-crystal and crystalline grains[4,12-14] imply high intrinsic J_c of individual grains, which is not reproduced in actual transport J_c measurements[3,6,7,10,11,15] in bulk polycrystalline materials presumably due to the weak links present at grain boundaries.[10]

We have previously reported structure densification in $YBa_2Cu_3O_{7-\delta}$ and some indication of J_c improvement by molten oxide processing.[7] In this paper, we report preliminary success in overcoming the weak-link problem through proper microstructural control using a modified molten oxide processing.

Precursor samples with a $YBa_2Cu_3O_{7-\delta}$ formula were prepared by mixing $BaCO_3$, Y_2O_3, and CuO in stoichiometric proportions, then repeatedly (four times) grinding, pressing, and sintering (900–950 °C for 16 h) in oxygen atmosphere. The samples were typically of rectangular bar or sheet shape, approximately 0.1–2×2×30 mm in dimensions. Transport critical currents were obtained from V-I characteristic curves using 0.2–2 μV/mm criterion. Lead wires were attached to the samples by In solder. The current was applied either by manual ramping or by pulsing from a capacitor bank ($\approx$6 ms decay times) and monitoring with a transient digitizer. Results for the two techniques were identical for the J_c measurement up to $\approx$3000 A/cm^2. Higher values of J_c were measured using the pulsing technique because of the sample and lead wire overheating problems in manual current ramping. The samples were melt processed by heating either to the single-phase liquid region (using local heating similar to that used in zone melting) or to the two-phase (liquid+solid) region. Shown in Fig. 1 is a portion of the approximate and qualitative sectional phase diagram[16,17] along the Y_2BaCuO_5-$YBa_2Cu_3O_{7-\delta}$ tie line. Four different temperatures were chosen for melt processing:

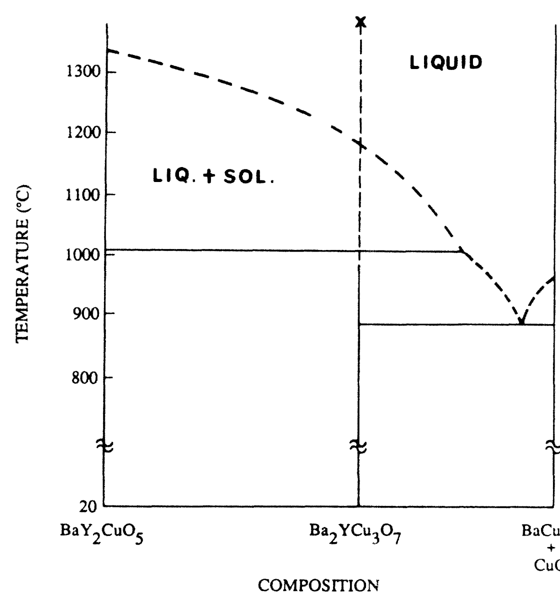
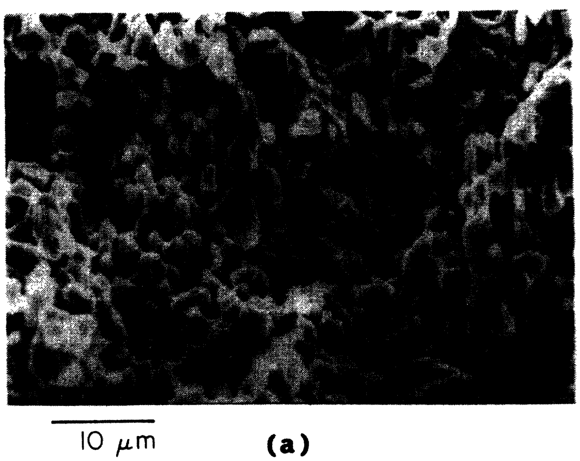


FIG. 1. Qualitative sectional phase diagram near the $YBa_2Cu_3O_{7-\delta}$ superconducting phase.

1320 °C (single-phase liquid), 1180 °C, 1110 °C, and 1030 °C (liquid+solid). Samples were held at each temperature for 0.5–120 min in flowing oxygen atmosphere, and then cooled in a temperature gradient of about 50 °C/cm to room temperature. (This processing is termed here as "melt-textured growth" following the manner in which the crystals are made to grow and align during solidification of the melt.) They were then given additional heat treatment afterwards[7] for purposes of homogenization, stress relief, and enhanced oxygen content.

Shown in Fig. 2(a) is a scanning electron microscopy (SEM) photomicrograph taken from the fracture surface of the conventionally sintered precursor samples. This as-sintered material (920 °C, 16 h, furnance cool, O_2) exhibits a granular, porous, and randomly oriented microstructure with an average grain diameter of about 5 μm and a density of about 90%. The transport J_c of the as-sintered material was 150–600 A/cm^2 at 77 K in zero field. These are far less than the theoretical upper limit set by the depairing critical current density (calculated from the critical-field and penetration depth values at 77 K, $J_c = H_c/3\sqrt{6}\pi\lambda \approx 5\times10^6$ A/cm^2). The J_c values of the sintered $YBa_2Cu_3O_{7-\delta}$ deteriorated exponentially in weak magnetic fields[11,15] (e.g., to about 1–10 A/cm^2 at $H = 1000$ G). Such a field dependence is far stronger than expected for a pinning-limited critical current by analogy with $A15$-type superconductors at comparable values of T/T_c, and could be explained by the presence of Josephson-type weak coupling between superconducting regions. These observations, together with the reported high magnetization J_c of single crystals ($\approx 2\times10^4$ A/cm^2 at 77 K),[12] suggest that the high-J_c grains in the sintered materials are decoupled by low-J_c regions presumably at grain boundaries.[10]



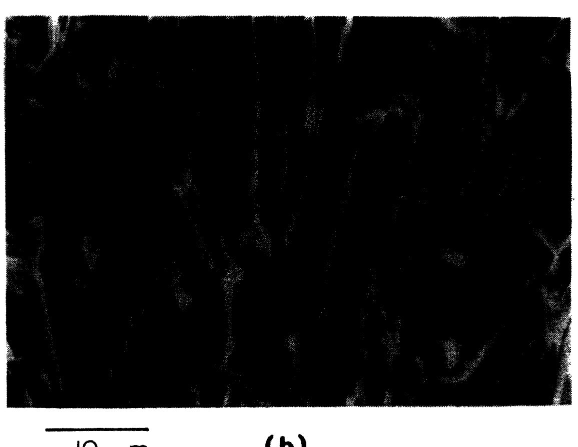


FIG. 2. Comparative SEM fractographs of (a) as-sintered and (b) melt-textured $YBa_2Cu_3O_{7-\delta}$.

A number of possibilities exist for the source of grain-boundary weak links: (i) conductivity anisotropy causing intrinsically weak connections at high-angle grain boundaries where a redistribution of currents is necessary, (ii) the presence of an insulating impurity layer (such as carbonates which forms easily in barium containing compounds), or other nonsuperconductive second phases, (iii) the presence of microcracks or stress concentration resulting from the severely anisotropic thermal expansion in different crystallographic directions, and (iv) deviation in chemistry or crystal structure at grain boundaries. The exact source of the weak-link behavior has not been conclusively identified for sintered $YBa_2Cu_3O_{7-\delta}$.

The melt-processed $YBa_2Cu_3O_{7-\delta}$ samples exhibit essentially 100% dense, locally textured, and needlelike microstructures [Fig. 2(b)] that are drastically different from the sintered structure of Fig. 2(a). The needles, identified to be the superconducting phase $YBa_2Cu_3O_{7-\delta}$ by energy dispersive x-ray analysis, optical and transmission electron microscopy, are typically $\approx$ 40–600 μm long and $\approx$ 2–5 μm in short dimensions. The needle axis appears to coincide with the a or b direction in the superconducting layer of the orthorhombic phase. Scanning electron microscopy at higher magnification shows fine parallel twins (characteristic of the tetragonal-orthorhombic transition). The adjacent needles seem to have only slight orientation change from each other (low-angle grain boundary), which is desirable for supercurrent flow in this anisotropically conductive compound. This type of structure resembles spherulitic crystals, which are often observed during solidification of liquid in materials having an anisotropic growth rate along different crystallographic orientations such as dichloro-diphenyl-trichloroethane (DDT).[18] The formation of spherulites consisting of many needlelike crystals from the liquid $YBa_2Cu_3O_{7-\delta}$ is apparently caused by the much higher crystal-growth rate in the a axis ($a = b$ in high-temperature tetragonal state) than in the c axis, which is further enhanced by the directional solidification employed in this work.

The drastic microstructural change presented in Fig. 2 is reflected as significantly altered superconducting properties, e.g., critical current density at 77 K. As shown in Table I, the transport J_c values (at $H = 0$) of the melt-processed $YBa_2Cu_3O_{7-\delta}$ are superior to those of the as-sintered samples. Also apparent from the table is the much improved J_c of the 1320 °C sample over the two-phase processed samples (1030 °C, 1110 °C, and 1180 °C), which is attributed to the minimal phase separation and trapping of nonsuperconducting phase (such as CuO-rich phase) between the spherulites.

Shown in Fig. 3 are the transport J_c (at 77 K) vs H

TABLE I. Transport J_c (77 K, $H=0$) of $YBa_2Cu_3O_{7-\delta}$. T_c ($R=0$) $=$91–93 K for all of these samples.

		J_c (A/cm^2)
As-sintered		150–600
Melted	1030 °C	1200–1700
	1110 °C	1000–1600
	1180 °C	1300–2000
	1320 °C	3100–7400

curves of the melt-textured $YBa_2Cu_3O_{7-\delta}$ as compared to the sintered materials. As is evident from the figure, the melt-processed material shows not only a dramatically improved transport J_c value of ≈ 7400 A/cm^2 at $H=0$ (as compared to about 150–600 A/cm^2 in the sintered structure) but also a considerably reduced dependence of J_c on magnetic fields, maintaining a substantial value of ≈ 1000 A/cm^2 (which is ≈ 3 orders of magnitude higher than the typical J_c values of ≈ 0.5–2 A/cm^2 in the sintered materials) at a reasonably high field of $H=10000$ G (1 T). The symptomatic property of the weak links, i.e., the extreme field dependence of J_c observed in the sintered structure, is thus no longer evident in the new structure.

While it is not possible at this time to definitely pinpoint the mechanism responsible for the suppression of the severe weak-link behavior, it is obvious that the high-temperature melt processing yields at least three beneficial structural changes simultaneously. These are (i) the formation of dense structure with enhanced connectivity between superconducting grains, (ii) the orientation of crystals along the preferred superconducting direction (a or b axis) in this anisotropically conductive layered compound, and (iii) the formation of new, cleaner grain-boundary area as the grain length increases (and the total grain-boundary area decreases) by 1–2 orders of magnitude, and as the decomposition of carbonate-type impurities (the presence of which has been suspected as one of the major possible sources of the grain-boundary weak links) is facilitated by exposure to the higher temperatures. It is most likely that these three factors serve as combined mechanisms responsible for the observed decrease in the magnitude of the weak-link behavior in the $YBa_2Cu_3O_{7-\delta}$ material prepared by the melt-textured growth.

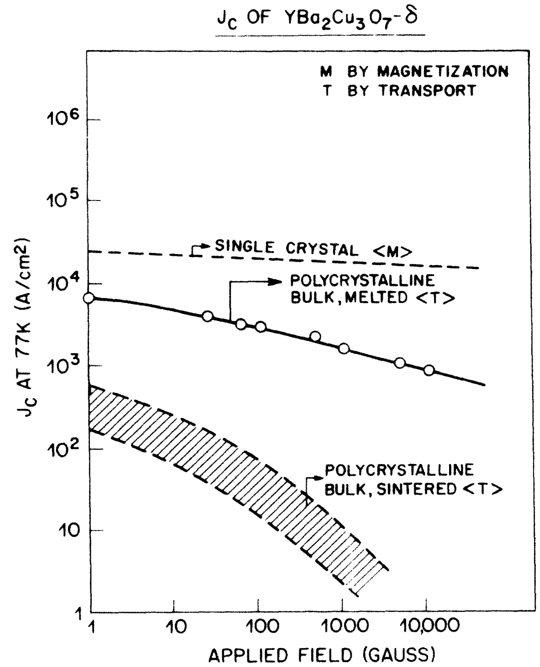


FIG. 3. Transport J_c vs H curves.

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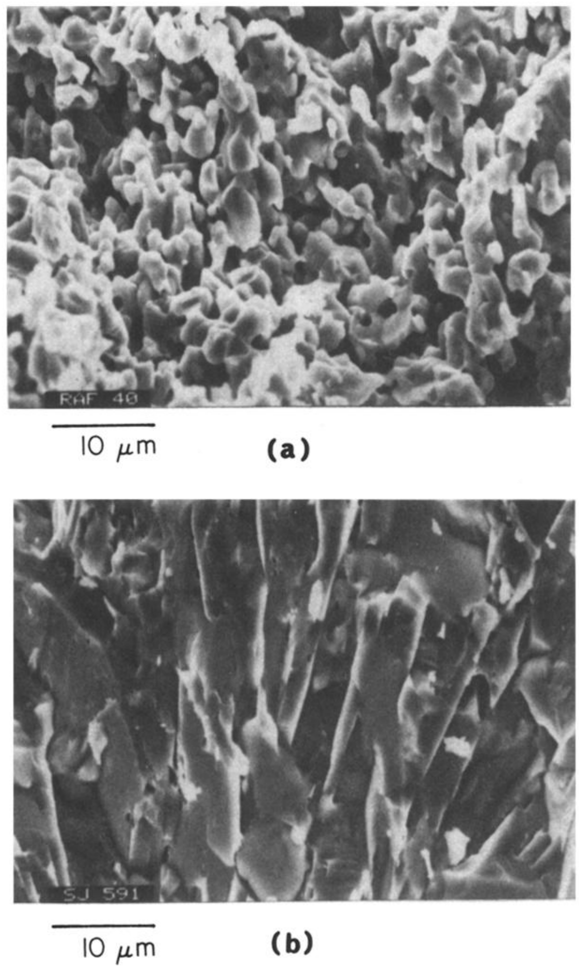

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