Enhanced high-field transport critical current density of superconducting bulk Y-Ba-Cu-O prepared by rapid solidification and directional annealing

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Strongly textured high-T_c bulk Y-Ba-Cu-O was prepared with rapid solidification and directional annealing processes. Sintered $YBa_2Cu_3O_7$ (1:2:3) samples, produced by conventional ceramic synthesis, were rapidly quenched with a twin rolling mill and directionally annealed by moving the sample at a speed of 0.2 cm/h through a temperature gradient of up to 60 °C/cm from 1020 to 900 °C. We have measured transport J_c of 2000 A/cm^2 by pulse current and 1150 A/cm^2 by dc at 77 K in a field of 15 T. It has been found that the J_c values measured by pulse and dc methods are approximately equal in high magnetic fields (8–15 T) and J_c measured by pulse current is larger than that measured by dc in magnetic fields below 8 T. The measured values of J_c decrease monotonically with increasing external magnetic field. Scanning and transmission-electron-microscopy studies showed that the 1:2:3 crystallites grow with their c axes perpendicular to the sample traveling direction. Crystallites of ~2–4 μm of Y_2BaCuO_5 (2:1:1) phase were observed also with their c axes perpendicular to the sample traveling direction. Grains with twin crystals orientated at ~90° from each other were observed. Precipitates of CuO were observed using energy-dispersive x-ray analysis. Dislocations with a density of $\sim 5\times 10^9$/cm^2 were found in the 1:2:3 crystals. These dislocations lie on the a-b plane. The enhancement of J_c probably is due to flux pinning by the dislocations and to the preferred orientation of the crystallites with the a-b plane parallel to the sample traveling direction.

I. INTRODUCTION

Since Jin[1–3] *et al.* developed the melt texture growth technique to enhance the critical current density (J_c) of high-T_c superconducting bulk $YBa_2Cu_3O_7$ (1:2:3), various methods have been extensively studied including "liquid phase processing" reported by Salama *et al.*,[4] Chen *et al.*,[5] and Yang *et al*,[6] "quench and melt growth" by Murakami *et al.*,[7] "melt texturing" by Alford and Button,[8] "continuous process by partial melting" by Meng *et al.*,[9] "powder melting process" by Lian *et al.*,[10] "unidirectional melt solidification" by Kase *et al.*,[11] and "zone melting" by McGinn *et al.*[12–16]

From these results the following factors favorable to large critical current became evident: (1) grains oriented so that the superconducting a-b planes also contain the long sample axis; (2) large superconducting grains; (3) high density; (4) low density of cracks; (5) precipitates such as Y_2BaCuO_5, CuO, and $BaCuO_2$; and (6) dispersion of fine defects and dislocations with dimensions on the order of a few hundred Å.

Kirk *et al.*[17] studied the effect of neutron-irradiation on flux pinning in single-crystal $YBa_2Cu_3O_{7-\delta}$. They reported the possibility of J_c enhancement by fine irradiation-induced defects on the order of a few hundred Å which serve as flux pinning centers.

Many other techniques have been applied to enhance current densities. It is recognized, however, that the transport J_c is suppressed in high magnetic fields at 77 K, e.g., $J_c = 16\,000$ A/cm^2 in 0 T and $J_c = 550$ A/cm^2 in 5 T for samples prepared by the powder melting process.[10]

We reported previously that the transport J_c of bulk Y-Ba-Cu-O has been enhanced by combining rapid solidification (RS) and directional annealing (DA) processings[18] to give $J_c = 4.3\times 10^4$ A/cm^2 in a magnetic field of 1 T at 77 K. The material was predominantly textured $YBa_2Cu_3O_7$ with a 20% volume fraction of Y_2BaCuO_5 (2:1:1 phase). Investigation of the high-field transport J_c, however, was not completed at that time. It is reported in this paper that strongly enhanced transport J_c values have been achieved in high magnetic field (0–15 T) at 77 K by optimizing the DA conditions.

The correlations between large high-field J_c and microstructure as characterized with transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are also discussed.

II. EXPERIMENTAL DETAILS

Strongly textured bulk Y-Ba-Cu-O was produced by rapid solidification (RS) and directional annealing, as described previously.[18] Pellets of $YBa_2Cu_3O_7$ prepared by conventional ceramic synthesis were rapidly quenched in a twin rolling mill (surface speed 11.5 m/s). After the RS process, a bar sample compacted with cold isostatic pressing was partially melted and directionally annealed

by slowly moving the sample through a sharp temperature gradient (60 °C/cm) from 1020 to 900 °C in air. At 1020 °C the sample consists of solid 2:1:1 phase and liquid Ba and Cu oxides. The sample was then cooled at 30 °C/h in flowing oxygen to establish optimal oxygen concentration. The DA apparatus consists of an open horizontal quartz tube of 2.3 cm inner diameter. A cooling jacket separates the hot zone and lower-temperature zone allowing a sharp temperature gradient to exist. The solidification rate of the liquid phase can be controlled by varying the sample speed and temperature gradient. It has been found that a gradient of 60 °C/cm and sample speed of 0.2 cm/h are required to produce the strongly textured specimen showing large transport J_c in high magnetic field. Typical sizes of bar specimens obtained by the above procedure are 0.5 cm in diameter and 6 cm in length.

Microstructure characterization of DA samples has been done with transmission electron microscopy (JEOL 2000 FX-II), scanning electron microscopy (Cambridge Instrument), energy-dispersive x-ray analysis (EDX, Cambridge Instrument), and x-ray diffractometry (XRD, Rigaku RU 300).

Samples for TEM were prepared by cutting disks of ~3 mm from longitudinal and transverse sections of the superconducting bar. The samples were prepared by mechanical grinding and subsequent ion milling using Ar^+ at 3 keV and an angle of ~15° to obtain perforation.

The electrical resistivity was measured on samples cut and then polished typically to 1 cm×0.4 mm×0.6 mm using a standard dc four-probe technique. The voltage contacts were typically 3–5 mm apart. Transport J_c measurements at 77 K in magnetic fields generated with a superconducting magnet were performed using continuous dc measurement as well as a pulse current technique. Contacts to the samples were made by soldering gold wires onto baked silver paint. The critical current density was determined using the $V=1$ μV ($E=2$–3 μV/cm) criterion. The dc and pulse current measurement systems are shown schematically in Fig. 1. A pulse current up to 125 A was generated by a series of power transistors or by a power supply (Kepco BOP-20M) controlled by a pulse generator (Tektronix PG 501). The pulse width was typically 10 μs with a repetition rate of 5 s^{-1}. The current and voltage drops across the sample were measured using a digital oscilloscope (Data Precision 6000). This system was capable of providing pulse widths ranging from a few microseconds to a few milliseconds. An important aspect of our pulse system was the electrical noise filtering system it employed. The continuous dc measurements were performed using a dc power supply of 24 A rating (Valhalla 2500 or Sorenson SRL 10-25), amplifier (Keithley 155), and an *X-Y* recorder (BBC Metrawatt SE780).

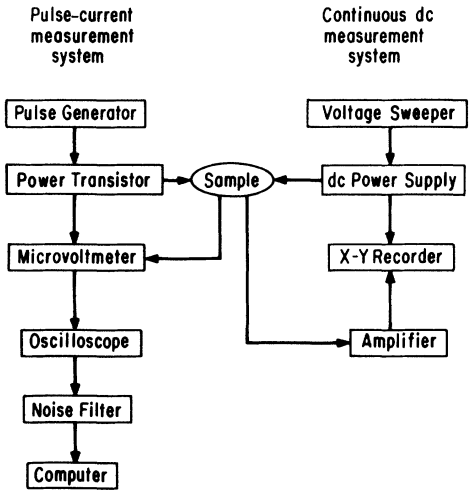


FIG. 1. Transport J_c measurement systems by pulse current and dc.

III. RESULTS AND DISCUSSIONS

A. Directionally annealed Y-Ba-Cu-O

Figure 2 shows powder XRD patterns of a DA sample. It is noted that the materials are predominantly $YBa_2Cu_3O_7$ (1:2:3) with a 25% volume fraction of Y_2BaCuO_5 (2:1:1). DA bar specimens were polished with diamond paste (0.3 μm), and their microstructures were examined with SEM and EDX. SEM micrographs of polished surfaces of a DA specimen are shown in Fig. 3. The surfaces are longitudinal [Figs. 3(a) and 3(b)] and perpendicular [Fig. 3(c)] to the bar axis, respectively.

The platelike grains seen on the longitudinal surface are up to 1 mm in length and show strong alignment [Figs. 3(a) and 3(b)]. In our previous work[18] it was reported that the *c* axes are strongly oriented normal to the bar length. The perpendicular surface of the bar specimen is shown in Fig. 3(c). The *a-b* planes, viewed edge on here, appear to have their normals randomly oriented in the plane normal to the bar axis. Some copper oxides remain in the DA specimens through peritectic reaction of 2:1:1 phase and liquid Ba and Cu oxides, as shown in Fig. 3(b). The typical DA sample showed a critical temperature $T_c(\rho=0)=91.9$ K.

B. Enhanced high-field transport J_c

Figure 4 shows typical *I-V* characteristics by pulse [Fig. 4(a)] or dc [Fig. 4(b)] measurements. Slopes of *I-V*

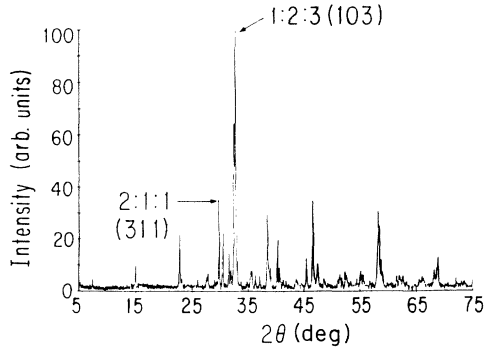
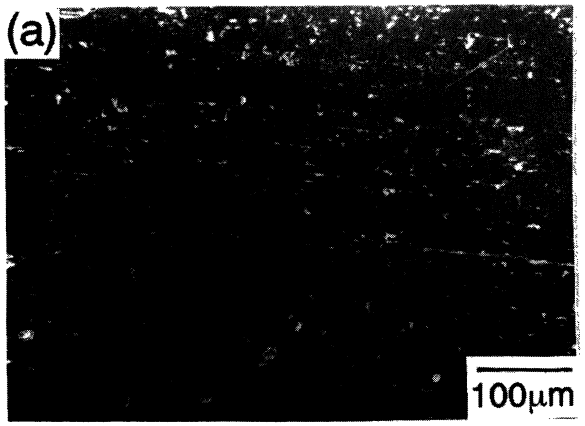
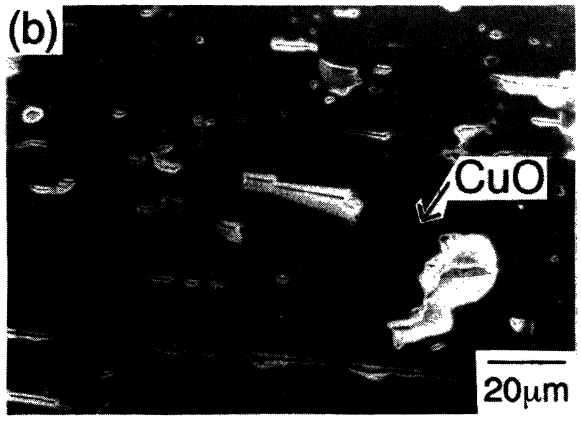


FIG. 2. X-ray-diffraction pattern of directionally annealed Y-Ba-Cu-O.

curves measured by the pulse current are sharper than those measured by dc. In either case the steep slope for $V<1$ μV shows that a more rigorous electric-field criterion (1 μV/cm instead of 2 or 3 μV/cm) would have negligible effect on the critical current density determined.

Figure 5 shows the dependence of critical current density on applied magnetic field. The square symbols in Fig. 5 represent pulse current J_c data at 77 K in magnetic fields up to 15 T. The magnetic field was applied normal to the direction of supplied current. Arrows in Fig. 5 mean subcritical current densities; i.e., a current density of 63 000 A/cm^2 in 0–2.5 T left the sample superconducting. The J_c values by pulse current leveled off between 8 and 15 T at a value of about 2000 A/cm^2.





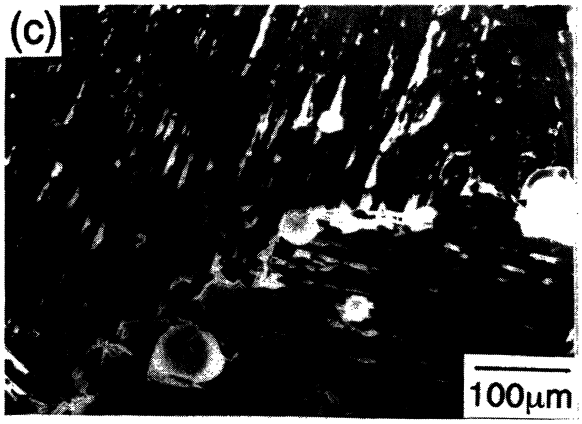


FIG. 3. SEM images of polished surface of directionally annealed Y-Ba-Cu-O: (a),(b) surface parallel to the bar axis and (c) surface perpendicular to the bar axis.

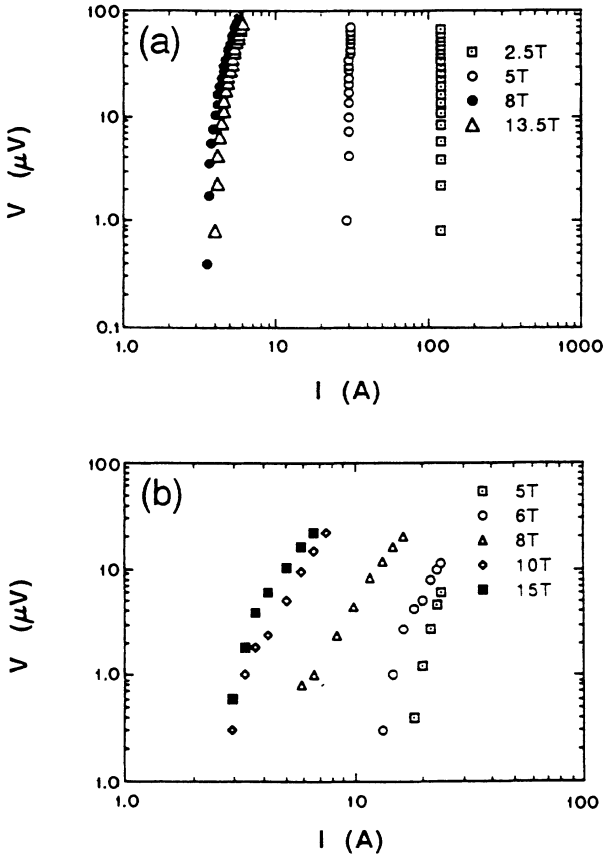


FIG. 4. *I-V* characteristic curves: (a) by pulse current and (b) by dc.

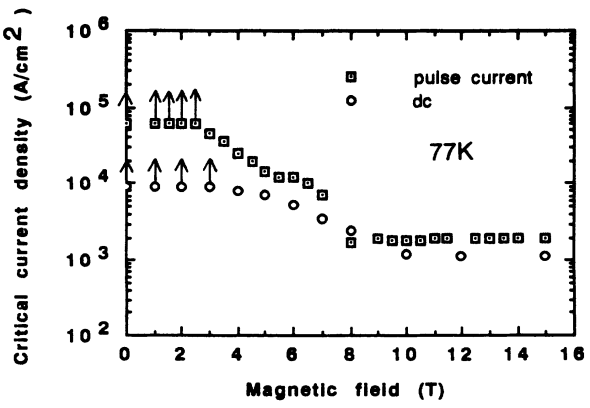


FIG. 5. Enhanced transport J_c of directionally annealed Y-Ba-Cu-O at 77 K in various magnetic fields up to 15 T. The magnetic field was applied perpendicular to J_c.

The dc transport measurements have also been made up to 25 A (circles in Fig. 5). Arrows again indicate subcritical current densities which leave the sample superconducting at 9100 A/cm^2 in 0–3 T. The dc measurements showed no significant decrease in J_c (1200 A/cm^2) over the field range from 9 to 15 T, and the continuous dc current of 3 A could pass through the DA sample in 15 T without a measurable voltage drop.

For fields from 8 to 15 T, there is little difference between the pulse and dc values of J_c. However, it is noted that in lower magnetic field ($B < 8$ T) pulse current values of J_c are larger than those by dc measurements.

C. Discussion

Figure 5 shows the familiar result that the critical current density varies inversely with the applied field. At low applied fields ($B < 3$ T), the current density saturates. This is not due to any physical phenomenon, but to the inadequacy of the current source used. The most interesting feature is that while J_c is similar for both types of measurements for $B > 8$ T, the results diverge for $B < 8$ T, the pulse field J_c being greater than the dc field J_c.

The simplest explanation for this is that Joule heating of the nonsuperconducting lead wires raises the sample temperature above the nominal 77 K of the LN_2 bath. The heating is clearly more severe for the dc measurement than the pulse measurement.

We are led to conclude therefore that the reduced J_c data at $B < 8$ T taken by dc measurements are flawed; the pulse data are representative of the true current carrying capability of the material at 77 K.

D. Microstructural characterizations with TEM

In order to determine the growth direction of the 1:2:3 crystallites with respect to the traveling direction of the bar, TEM studies were carried out on samples cut perpendicular (cross section) and parallel (longitudinal) to the traveling direction. TEM studies were also carried out to detect the presence of precipitates and defects in the sample and to investigate their role in the enhancement of J_c.

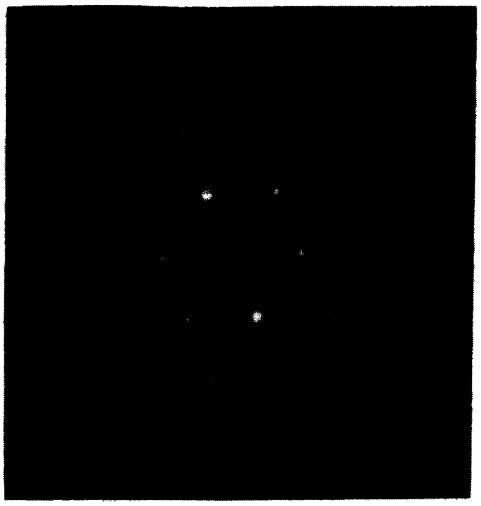


FIG. 6. (431) electron-diffraction pattern of a 1:2:3 crystal obtained from a cross-sectional sample. The c axis of the 1:2:3 phase makes an angle of $\sim 86.2°$ with the plane normal, indicating that the 1:2:3 phase grows with the c axis perpendicular to the traveling direction of the sample.

Figure 6 shows a (431) electron-diffraction pattern of a 1:2:3 crystal obtained from a cross-sectional sample. The direction normal to this pattern and parallel to the axis of the bar makes an angle of $\sim 86.2°$ with the c axis of the 1:2:3 phase. This indicates that the c axis lies approximately perpendicular to the traveling direction, and therefore the longitudinal axis of the bar lies in the a-b plane of the 1:2:3 phase. Most of the diffraction patterns obtained from different areas of the cross-sectional sample showed either (431) and (341) or $(1\bar{3}1)$ and $(3\bar{1}1)$ electron-diffraction patterns of the 1:2:3 phase. All of these diffraction patterns have a normal direction at an angle of $\sim 84°$–$86°$ with the c axis of the 1:2:3 phase, indicating that most of the crystals have their c axis perpendicular to the bar axis. This result is in agreement with the x-ray-diffraction data obtained from a longitudinal sample, cut parallel to the bar axis, which show mostly (001) reflections, as reported earlier.[19] Even though the c axis in the 1:2:3 crystallites is approximately perpendicular to the bar axis, the a and b axes were not observed to be parallel to the bar axis. The smallest angles made by either a or b with the normal to the diffraction patterns are $\sim 37°$ between a and $\langle 431 \rangle$ or between b and $\langle 341 \rangle$, and $\sim 19°$ between b and $\langle 1\bar{3}1 \rangle$ or between a and $\langle 3\bar{1}1 \rangle$.

In addition to the 1:2:3 phase, 2:1:1 crystallites with dimensions 3–4 μm by 1.5–2 μm were identified from electron-diffraction patterns and EDX spectra. It is interesting to note that the 2:1:1 precipitates also were aligned with their c axes perpendicular to the bar axis. However, in the case of the 2:1:1 crystals, either the $\langle 100 \rangle$ or $\langle 010 \rangle$ directions were parallel to the bar axis. Because the sizes of the 2:1:1 and CuO precipitates are much larger than either the typical coherence length or the separation of flux lines in $YBa_2Cu_3O_7$, we believe that they cannot act as flux-pinning centers. We have not observed evidence for other precipitates such as $BaCuO_2$ or Y_2O_3, in addition to the 2:1:1 and CuO precipitates, which could be responsible for flux pinning and high J_c values.

Figure 7 shows an intragrain microcrack ~ 1.8 μm long and 0.07 μm wide. This microcrack runs perpendicular to and through several twins in a 1:2:3 crystal. The cause of the crack is not clear at the present moment, but it was probably produced during growth or during sample preparation for TEM. It can be seen in this figure that some twins are wider than others, but have a periodicity of approximately 1200 Å.

Figure 8 shows a bright field image of a 1:2:3 crystal obtained from a sample cut parallel to the bar axis. The crystallite is oriented approximately with the $\langle 001 \rangle$ direction parallel to the electron beam. This figure shows dislocations lying in the a-b plane with a density of 5×10^9/cm^2. The figure also shows dislocation loops (marked by arrows) in some of the twins. Because the strain around a dislocation extends to ~ 200 Å and be-

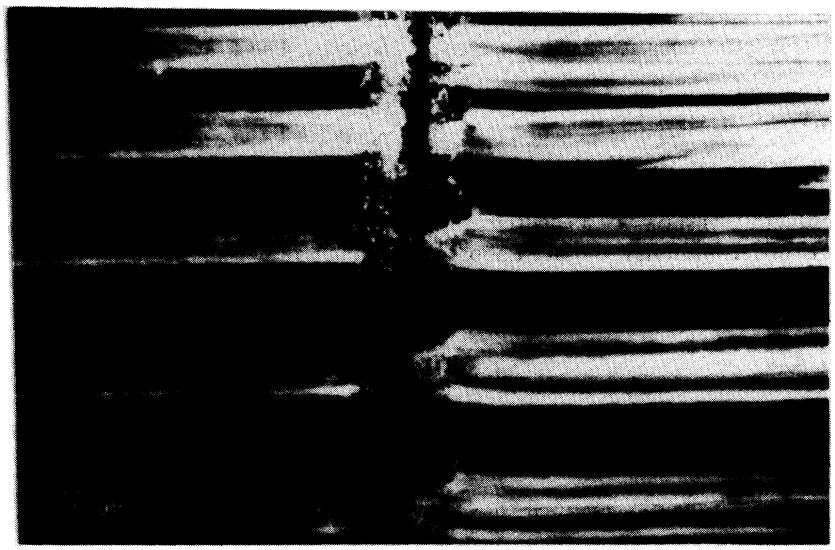


FIG. 7. Microcrack observed inside a 1:2:3 crystal. The crack runs perpendicular to and through several twins within the crystal.

cause the dislocations in the 1:2:3 phase lie on the *a-b* plane, we believe that they may act as flux-pinning centers, as has been previously suggested.[20] These dislocations may, therefore, contribute to the enhancement of J_c.

IV. SUMMARY

Strongly textured bulk superconducting Y-Ba-Cu-O was produced by rapid solidification and directional annealing. The resulting material was predominantly $YBa_2Cu_3O_7$ with a 25% volume fraction of Y_2BaCuO_5. The *c* axes of the 1:2:3 phase were strongly oriented normal to the longitudinal direction. Directionally annealed Y-Ba-Cu-O showed transport J_c in excess of 63 000 A/cm^2 in 0 T and $J_c = 2000$ A/cm^2 in 15 T at 77 K with pulse current measurements.

Transport J_c was also measured with the continuous dc method and indicated a J_c in excess of 9100 A/cm^2 in 0 T and 1200 A/cm^2 in 15 T at 77 K.

Microstructural characterization using transmission electron microscopy showed the presence of 2:1:1 precipitates of $\sim 2-4$ μm in size. Also, an intragrain microcrack was observed to run through several twins, and in some regions twins in two directions were observed. Dislocations were observed in the *a-b* plane of the 1:2:3 grains, and they may act as strong pinning centers responsible for the high J_c values measured in these samples.

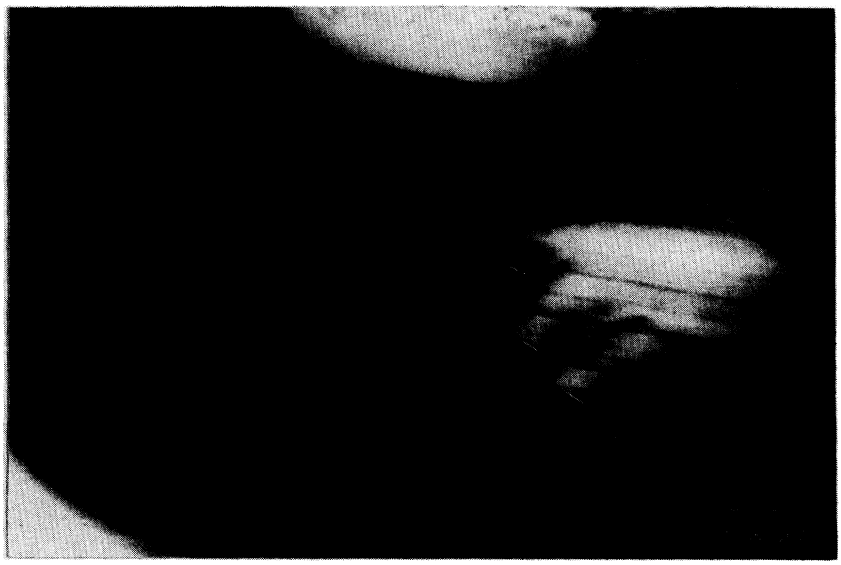


FIG. 8. Bright field image of a 1:2:3 crystal showing dislocations. Dislocation loops, marked by arrows, are observed in some of the twins.

Additional efforts to understand the role of strong flux pinning and enhanced transport current density are required.

ACKNOWLEDGMENTS

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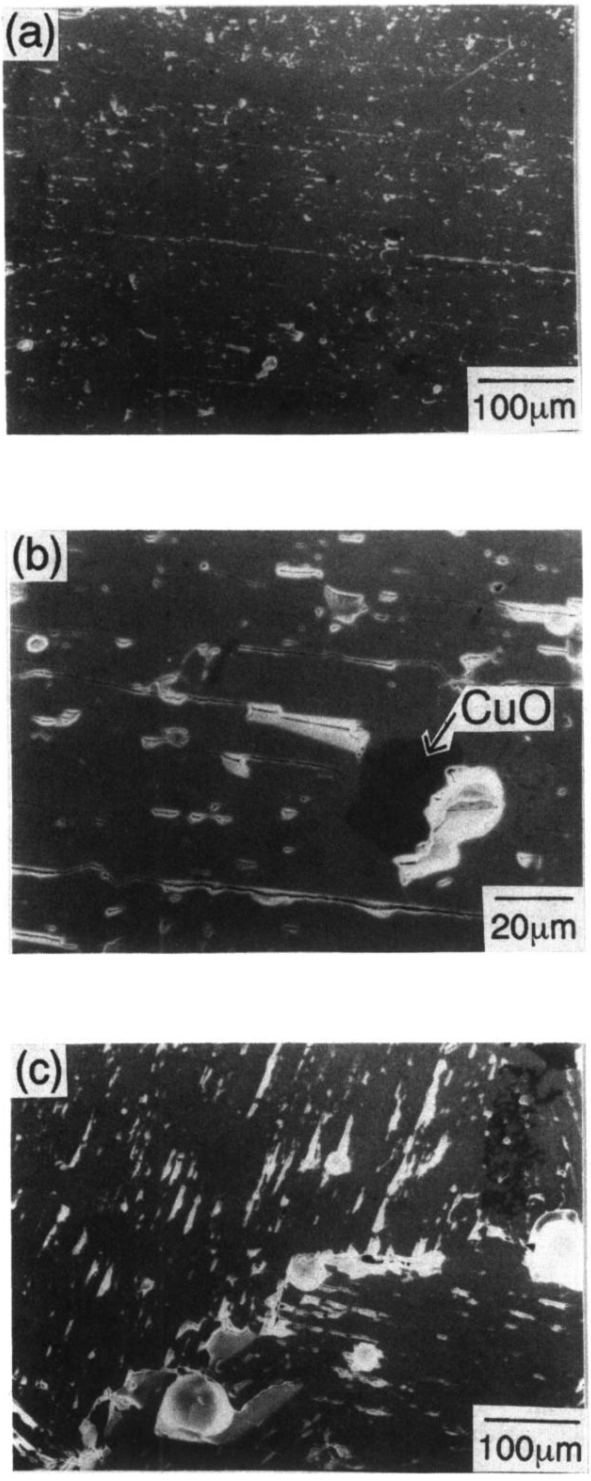


FIG. 3. SEM images of polished surface of directionally annealed Y-Ba-Cu-O: (a),(b) surface parallel to the bar axis and (c) surface perpendicular to the bar axis.

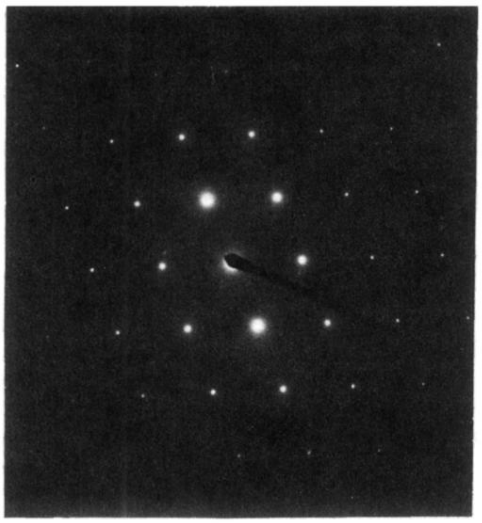


FIG. 6. (431) electron-diffraction pattern of a 1:2:3 crystal obtained from a cross-sectional sample. The c axis of the 1:2:3 phase makes an angle of $\sim 86.2°$ with the plane normal, indicating that the 1:2:3 phase grows with the c axis perpendicular to the traveling direction of the sample.

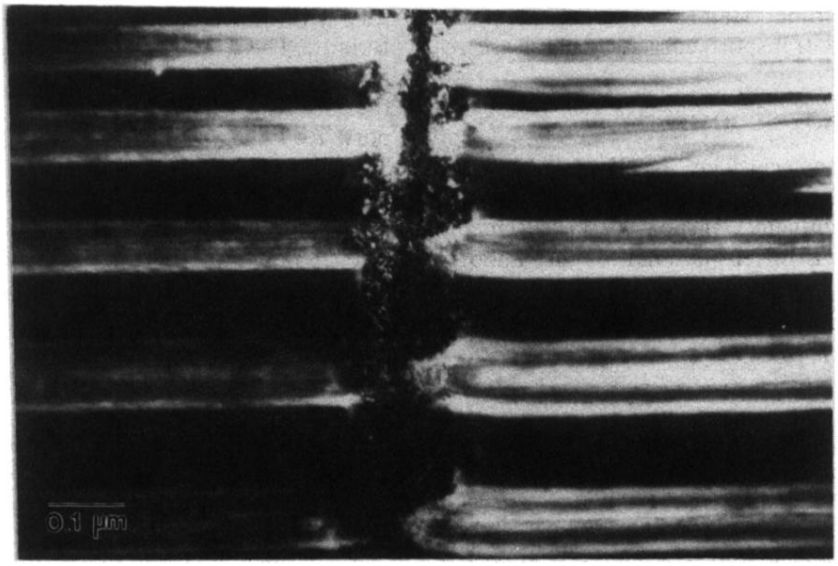
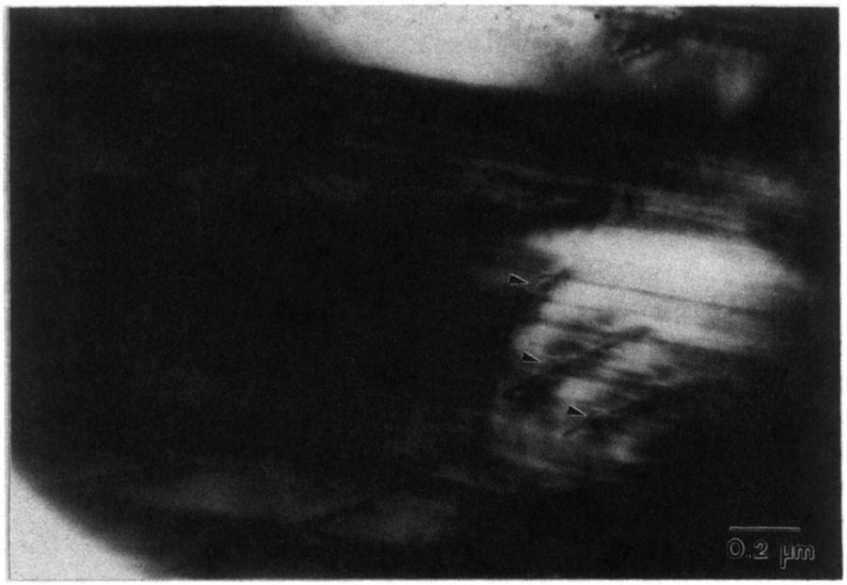


FIG. 7. Microcrack observed inside a 1:2:3 crystal. The crack runs perpendicular to and through several twins within the crystal.



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