larger than that of the matrix owing to their higher aluminium concentrations, so the diffuse scattering peak would be found at a slightly lower angle than the Bragg reflection position, in agreement with our observation. This accords with the Suzuki lock interpretation of Epperson, Fürnrohr & Ortiz (1978) for their X-ray results, and with the transitory increase in mechanical strength noticed by Saarinen (1968) and Chirikov (1972) on subjecting α-CuAl to heat treatments similar to our 2 min anneal.

Quenching from 723 K was found to be sufficient to produce plastic deformation in a Cu-14·76 at.% Al alloy specimen 22 mm wide and 3 mm thick (Epperson, Fürnrohr & Ortiz, 1978) but may not be when an imperfect *in situ* 'quench' is made of an electron-microscope specimen, as in our case.

From the results of their analysis of the temperature behaviour of Shockley partial dislocations in Cu-13·43 at.% Al, Saka, Sueki & Imura (1978) concluded that no definitive evidence could be found for the existence of a Suzuki effect, but their annealing times were all much longer than 2 min, which is thought to correspond to the time constant of the 'rapid process' observed in this alloy system in the study of the order/disorder kinetics of notionally inhomogeneous phases conducted by Trieb & Veith (1978).

A careful series of electron diffraction patterns from several short-anneal specimens taken near the matrix critical voltage (possibly including imaging and energy filtering) is likely to help clarify the situation.

We thank Professor Sir Peter Hirsch FRS for the provision of laboratory facilities in Oxford. JRS acknowledges useful discussions with Professor J. M. Cowley FAA, FRS.

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Grain Boundaries in Sintered $YBa_2Cu_3O_{7-\delta}$

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(*Received* 14 *December* 1987; *accepted* 8 *March* 1988)

Abstract

High-resolution electron microscopy has been carried out on grain boundaries of 92% dense $YBa_2Cu_3O_{7-\delta}$ in the tetragonal form. Grain boundaries were found to be predominantly parallel to (001) of one of the adjacent grains. No amorphous interlayer was observed at the grain boundaries. At some grain boundaries highly localized strains were detected.

Introduction

$YBa_2Cu_3O_{7-\delta}$, prepared using different routes (oxides, nitrates, oxalates), shows a density in the range of 50-70%. Because this material is very brittle an obvious goal is to densify the material as much as possible. Another reason for densification is a decrease in decomposition which was found to start at the surface (Zandbergen, Gronsky & Thomas, 1988).

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A disadvantage of highly dense materials seems to be the very slow uptake of oxygen. For densities of 90% and more this requires progressively more than one day of annealing at 720 K.

The critical current is found to depend strongly on the alignment of the grains. Jin *et al.* (1987) obtained an increase of two orders of magnitude by alignment of the grains. It is to be expected that for further improvements in the critical current in sintered polycrystalline samples engineering of the grain boundaries will play a major role. Consequently, detailed studies of the grain boundaries are very important in order to understand differences in defect-sensitive macroscopic behavior (*e.g.* critical current) of various specimens.

An investigation of grain boundaries was started, which addressed a number of problems: (*a*) the role of grain boundaries in the (obstruction of) oxygen transport, necessary for the transformation from tetragonal to orthorhombic; (*b*) the role of grain boundaries as possible constraints in this transformation and the resulting structural deformations; and (*c*) the correlation of bulk behavior and the structure at and near the grain boundaries (*e.g.* the presence of an amorphous interlayer and the existence of stress-induced structural changes).

Although the research was started recently, a number of interesting results were obtained, which are presented in this paper.

Experimental

Specimens were prepared by heating pressed pellets at 1220 K for several hours. The pellets were pressed at 2400 p.s.i. ($1{\cdot}687\times10^6$ kg m^{-2}) from $YBa_2Cu_3O_{7-\delta}$ with no additives, obtained by heating in the temperature range of 1120–1150 K for 12–6 h respectively. With this method 88–92% dense material was obtained.

Although most samples were annealed at 720 K for 2–40 h, sometimes the uptake of oxygen indicated that a considerable part of the material did not transform to $YBa_2Cu_3O_7$ and remained oxygen deficient.

Since the major interest in this part of our studies concerns the structure of the grain boundaries of the tetragonal as well as the orthorhombic modification of $YBa_2Cu_3O_{7-\delta}$, all materials were prepared as dense as possible. The results on grain boundaries presented in this paper are from the tetragonal modification. However, the principles learned should also apply to the orthorhombic modification.

For high-resolution electron microscopy, specimens were thinned by ion milling. First a pellet was thinned to approximately 10 mm with dry 400 mesh grinding paper. Next a piece of about 2 × 2 mm was glued on a copper slot grid with silver epoxy. Ion milling was carried out with Ar of 4 keV at an incidence angle of 12°. The sample was liquid-nitrogen cooled. After a hole was obtained the thinning was stopped but the sample was left in the vacuum of the ion milling equipment. When the electron microscope was ready, the sample was taken out of the vacuum and immediately placed inside the microscope to minimize possible damage or chemical change (Zandbergen, Hetherington & Gronsky, 1988).

High-resolution electron microscopy was carried out with the Berkeley Atomic Resolution Microscope (Gronsky & Thomas, 1983), equipped with a ±40° double tilt/lift goniometer operating at 800 or 1000 kV. Image processing to improve the signal/noise ratio of several high-resolution images was performed using *SEMPER* software (Saxton, 1978).

Results

A large number of grain boundaries show the interface of one of the grains to be a (001) plane which must be a low-energy plane. The orientation of the grain is expected to be random if the process of growth and densification occurs by impingement of grain upon grain. That is, specific orientation relationships are not developed, so new grains do not grow from existing ones but simply coarsen and impinge even while favoring (001) facets. No indications for a preferred orientation were found. In Fig. 1 an example is given of a grain boundary in which the interface of one of the grains is (001). The other grain is not at 90° so it is not a [100] 90° rotation twin as described by Zandbergen, Gronsky, Chu, DeJonghe, Holland & Stacey (1987) but a randomly oriented grain. Fig. 2 shows a triple point with two grains with their (001) planes parallel to the grain boundaries. In neither case is there any grain boundary phase so there is probably no liquid sintering.

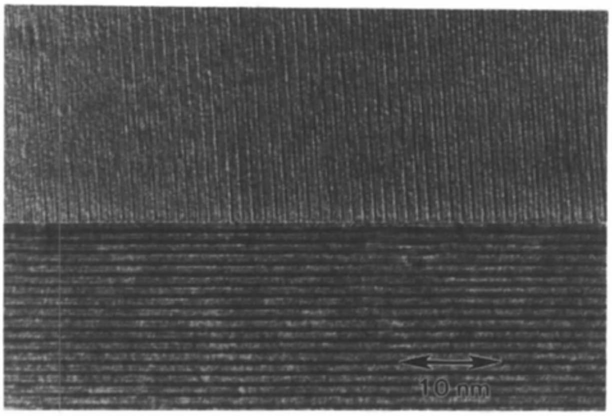


Fig. 1. High-resolution image of a grain boundary in tetragonal $YBa_2Cu_3O_{7-\delta}$ specimen. Both grains have their *c* axis in the plain of the image but are not orthogonal. No intergranular phase is observed at the grain boundary.

In both cases the images do not show high-resolution details perpendicular to the *c* axis. This is because the specimen had to be tilted out of the low-index orientation in order to image such that the [001] directions of both grains were parallel to the image plane. This does not allow orientation of one of the grains along [100], [010] or [110], which is a requirement for the imaging that resolves atomic details. Nevertheless, the availability of the large tilt (±40°) stage in the Berkeley Atomic Resolution Microscope is extremely useful for these analyses, because grain boundaries should be imaged edge-on in order to be sure whether intergranular phases do or do not exist.

Discussion

One of the most widely studied problems over the last decade has been that of grain boundary interfaces (Thomas, 1988) in sintered and hot-pressed compacts which often require sintering aids to allow liquid-phase sintering. Well known examples are the covalent materials silicon carbide, silicon nitride as well as ionically bonded alumina, zirconia/mullite *etc.* and electronic materials such as ferrites and ferroelectrics.

Although the grain growth in $YBa_2Cu_3O_{7-\delta}$ is different from many of the materials mentioned above in that liquid phases are not involved, nevertheless much can be learned from this well studied material. Furthermore, engineering of $YBa_2Cu_3O_{7-\delta}$ to align the grains might involve higher processing temperatures (Jin *et al.*, 1987), which implies the presence of liquid phases.

In all materials, the presence of amorphous material at the grain boundaries will lead to a deterioration of the properties, as is illustrated in Fig. 3. Analogous to the loss of ionic conduction in Na β-alumina polycrystals, the non-coincidence of the (001) electron conduction plane in the $YBa_2Cu_3O_{7-\delta}$ phase shown in Figs. 1 and 2 immediately suggests that this is an important factor in the low critical currents observed in these superconductors. The increase in the critical current of two orders of magnitude for well aligned grains (Jin *et al.*, 1987) is in accordance with this expectation.

The presence of strain, however, is expected to lead to contrary effects when comparing superconductors with other ceramics. For zirconia/mullite systems, the strain at the grain boundary can contribute to improved mechanical properties such as toughness by microcracking, or lead to the martensitic tetragonal–monoclinic transformation toughening in

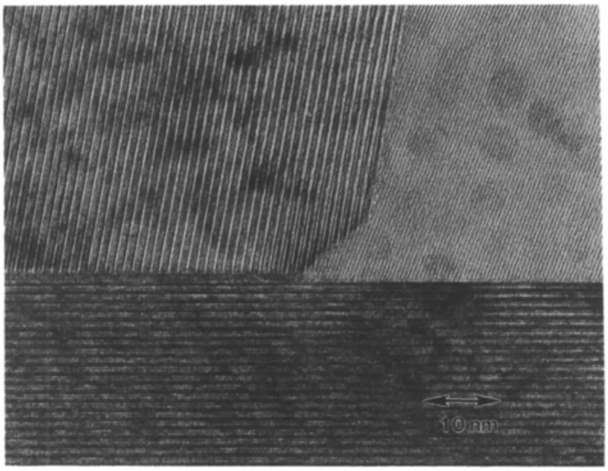
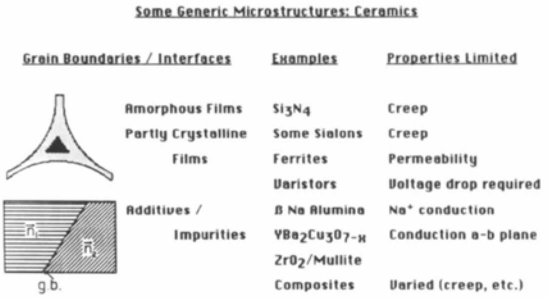


Fig. 2. High-resolution image showing a triple point of grain boundaries. The grain boundaries are all parallel to (001) planes of one of the adjacent grains except for the truncation near the center of the figure.



Some Generic Microstructures: Ceramics

Grain Boundaries / Interfaces	Examples	Properties Limited
Amorphous Films	Si_3N_4	Creep
Partly Crystalline	Some Sialons	Creep
Films	Ferrites	Permeability
	Varistors	Voltage drop required
Additives /	β Na Alumina	Na^+ conduction
Impurities	$YBa_2Cu_3O_{7-x}$	Conduction a-b plane
	ZrO_2/Mullite	
	Composites	Varied (creep, etc.)

Fig. 3. Schematic summary showing generic microstructures at grain boundaries and interfaces in a wide range of ceramics.

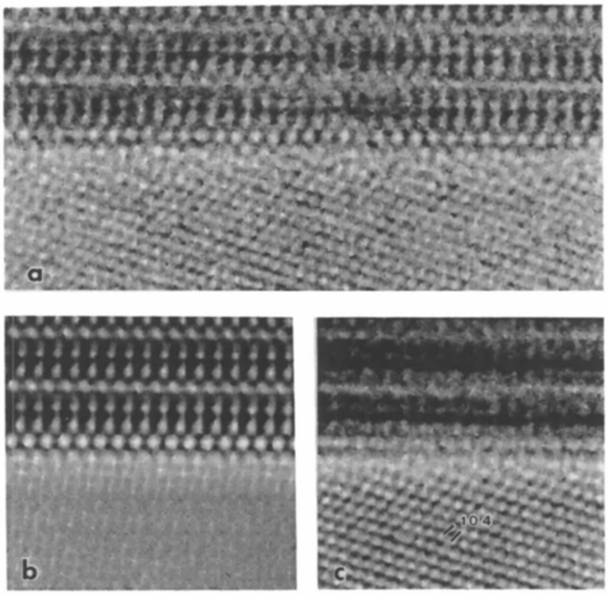


Fig. 4. Digitized high-resolution image of a grain boundary: (*a*) the upper grain is in [100] and the lower grain in [441] orientation; (*b*) and (*c*) show images averaged along the grain boundary. Note the bending of the (104) lattice planes in the lower grain near the grain boundary, indicating localized strain fields.

partially stabilized zirconia phases (Evans & Cannon, 1986). In superconductors, local changes in structure may lead to unfavorable copper–oxygen configurations which can have strong effects on the critical current, because its magnitude is determined by the critical current of the grain boundaries and their strained surroundings.

At present there are not enough data to quantify the occurrence and the magnitude of strain, and thus direct correlation with the critical current data is not possible. However, high-resolution electron microscopy shows that the strain is highly localized near the grain boundary (see Figs. 4 and 5). Research will be continued on these strain observations in both the orthorhombic and tetragonal forms.

In summary, we have found that dense polycrystalline $YBa_2Cu_3O_{7-\delta}$ materials prepared by sintering of pressed pellets without sintering aids develop random grain boundaries, but highly faceted along (001). There are no observed second phases, but sometimes highly localized strain fields at the grain boundaries. The structural discontinuities observed may very well explain the low critical currents obtainable in polycrystalline superconductors which have randomly oriented grains.

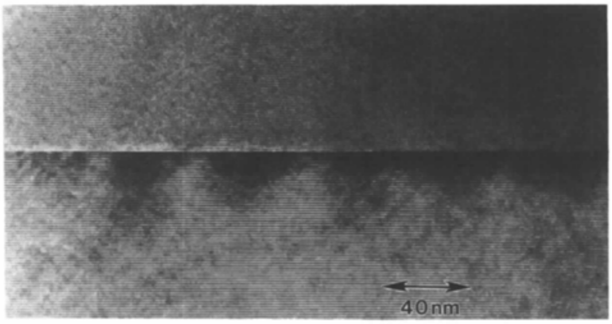


Fig. 5. Grain boundary of two grains approximately in [110] (top) and [100] (bottom) orientation. At each position where a unit cell of the top grain ends at the boundary, a strain center occurs in the bottom grain. This indicates that the upper grain grew to impingement on the lower grain.

The authors thank M. Y. Chu and Dr L. C. DeJonghe for providing the specimen. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, US Department of Energy, under contract No. CE-AC03-76SF00098.

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Acta Cryst. (1988). **A44**, 775–780

A Contribution to the Unsolved Problem of a High-Tilt Fully Eucentric Goniometer Stage

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(*Received* 30 *November* 1987; *accepted* 17 *March* 1988)

Abstract

A design is presented of a high-angle fully eucentric tilting stage (±45, ±23° around two orthogonal axes) for a transmission electron microscope. The concurrent design of suitable objective-lens pole pieces has been made in order to get the best compromise between electron optical performances and the difficulties inherent in the construction of the stage. A resolution of 3 Å is calculated at an accelerating voltage of 200 kV. The design exploits the space both above and in the middle of the objective pole-piece

0108-7673/88/060775-06$03.00