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Demonstration of Grain Growth Induced Microcracking and its Role in the Electrical Response of $YBa_2Cu_3O_{7-\delta}$

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Abstract

The effect of grain size on the electrical properties of polycrystalline $YBa_2Cu_3O_{7-\delta}$ has been investigated A strong decrease in the critical current density has been observed when an average grain size of 15 μm is exceeded Large grains promote microcracks due to anisotropic volume changes during cooling from the sintering temperature This causes a reduction in the effective current-carrying cross section of the material Ultrasonic measurements were used to confirm a significant increase in the microcrack density for large grained samples

Der Effekt der Korngroße auf die elektrischen Eigenschaften von polykristallinem $YBa_2Cu_3O_{7-\delta}$ wurde untersucht Es wurde ein starker Abfall der kritischen Stromdichte beobachtet, wenn die mittlere Korngroße von 15 μm uberschritten wurde Große Korner verursachen Mikrorisse aufgrund ihrer anisotropischen Volumenanderung wahrend des Abkuhlens von der Sintertemperatur Hierdurch wird die stromtragende Querschnittsflache des Materials reduziert Mittels Ultraschall konnte die Mikrorißbildung in Proben mit grobkristallinem Gefuge deutlich erhoht werden

On a étudié l'effet de la taille des grains sur les propriétés électriques du $YBa_2Cu_3O_{7-\delta}$ polycristallin On a observé une forte décroissance de la densité de courant critique lorsque la taille moyenne des grains dépasse 15 μm Les gros grains provoquent des microfissures en raison de changements volumiques anisotropiques durant le refroidissement à partir de la température de frittage Celà entraîne une réduction de la section conductrice efficace du matériau Des mesures par ultrasons ont confirmé une augmentation significative de la densité des microfissures dans les échantillons à gros grains

1 Introduction

Since the discovery of superconductivity in copper based oxides by Bednorz and Muller,[1] the microstructure has been shown to have an important role for the properties of this type of material [2] The critical current density measured at 77 K and in 'zero' field (j_c) has been widely used as the appropriate and convenient index of material quality for $YBa_2Cu_3O_{7-\delta}$ and its relatives which exhibit superconductivity above this temperature This is because many proposed applications require high current densities greater than 10^5 A/cm^2 However j_c is strongly influenced by the method and details of preparation relating directly to the microstructure For example, thin films carry critical currents greater than 10^5 A/cm^2, (Ref 3) whereas bulk ceramics yield values for j_c typically in the range 10^2–10^3 A/cm^2 These lower critical current densities in bulk ceramics are explained by the presence of weak links separating superconducting regions

Several types of defect in the microstructure may contribute to weak link behaviour The materials are in essence two-dimensional conductors (or superconductors) and the mismatch of grains which will occur in a microstructure with random grain orientations decreases j_c [4] At the grain size scale, impurities, second phases, and reduced contact area in a porous ceramic will also play a significant role Transmission electron microscope (TEM) studies have shown the presence of structural defects such as intergrowths and twinning,[5] suggesting another possible source of weak links at the scale of a few

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atomic distances The separation of the effects of these different imperfections in the ceramic microstructure presents an intriguing and technologically important problem

In this communication we focus attention on geometrical aspects of the microstructure and, in particular, on the effect of microcracking on the electrical properties of large grained $YBa_2Cu_3O_{7-\delta}$

2 Experimental

2.1 Preparation

Bulk ceramic samples were prepared using standard procedure This involves grinding the stoichiometric mixture of Y_2O_3, CuO, and $BaCO_3$ powders by hand with mortar and pestle, calcination at 940°C, and sintering of the pressed disc at 975°C in air The purity of the starting powders was 99 99% or greater X-ray diffraction measurements indicated minor quantities of CuCO and $BaCuO_2$ in the calcined product The firing cycle also includes an annealing step at 600°C followed by slow cooling (1°C/min) down to room temperature Some of the samples were reannealed in oxygen at approximately 500°C to promote the tetragonal to orthorhombic transformation

2.2 Characterization

Densities of sintered material were evaluated using Archimedes' principle The microstructure was examined by scanning electron microscopy and the average grain size was estimated with Jeffries procedure For electrical characterization, samples were cut and polished in the form of thin bars, typically 1 1 cm long with a cross sectional area of 0 01–0 02 cm^2 The room temperature resistivity and the current–voltage behaviour at 77 K in 'zero' magnetic field were measured using a four-terminal configuration. 'Zero' field refers to zero applied field but includes the presence of the Earth's magnetic field of approximately 0 5 × 10^{-4} T Electrical contact was achieved using silver epoxy paint which yielded an electrode resistance of less than 5 Ω reproducibly Heating effects on the current carrying terminals were minimized by immersion of the sample in liquid nitrogen The critical current density was evaluated using a criterion of 1 μV/cm between the voltage sensing electrodes

3 Results and Discussion

Dilatometry was used to establish that significant densification resulted for samples sintered at 975°C Previous work showed that the microstructure evolves as a function of sintering time by (i) grain growth, and (ii) change of grain shape from long thin rectangular shaped grains to a more rounded and equiaxed form [6] These changes can be explained by the involvement of a liquid phase during sintering due to the presence of residual CuO after the calcination step.

Samples were sintered for different durations in order to study the effect of grain growth on the electrical properties The density, grain size, and room temperature resistivity, ρ_{300}, measurements are summarized in Table 1 For sintering times of 20 h and longer, the density of the samples is constant within error, and therefore, this factor should not influence the data significantly Reannealing the samples in oxygen leads to higher values of J_c due to an increase in oxygen content (Fig 1) For both air annealed and oxygen reannealed samples, the increase of grain size has little apparent effect on J_c and ρ_{300} for sintering times up to 45 h If any trends exist they can be explained by a slight increase in density between 10 h and 20 h sintering, or they are obscured by the scatter of the data However samples which are sintered for 60 h exhibit a pronounced drop in J_c with a parallel increase in ρ_{300} Furthermore, the air annealed, and oxygen reannealed samples have similar values of J_c, suggesting the oxygen content is no longer different between the two sets of samples.

The simplest explanation is that microcracking

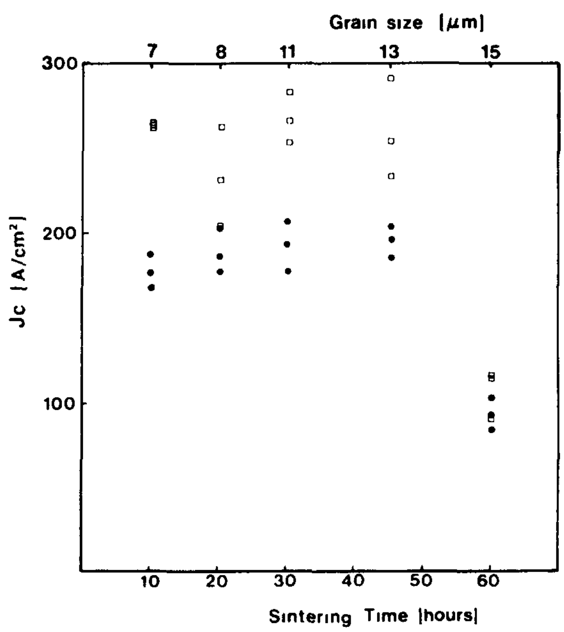
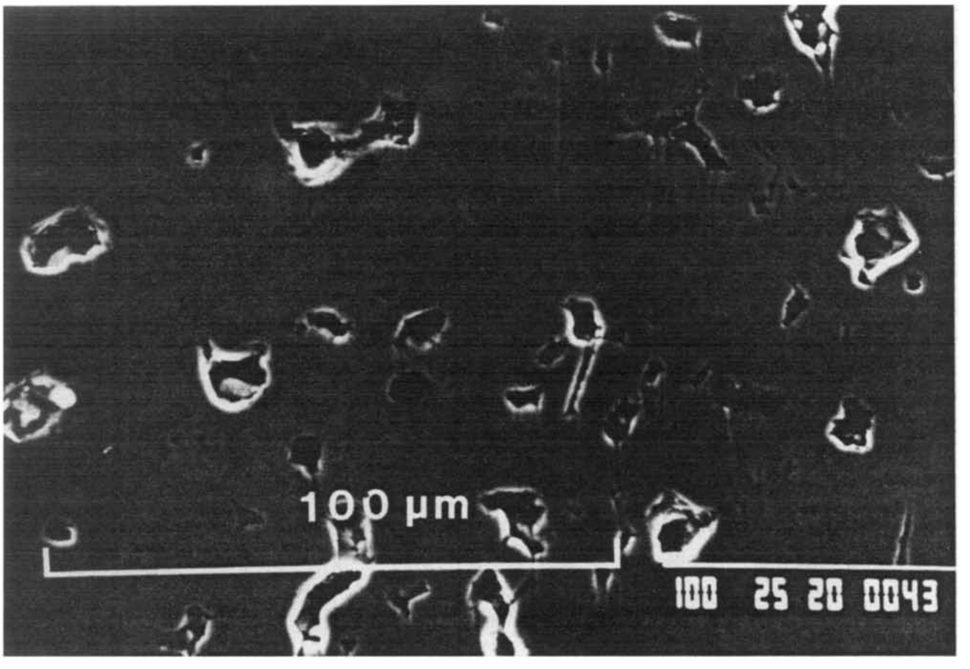


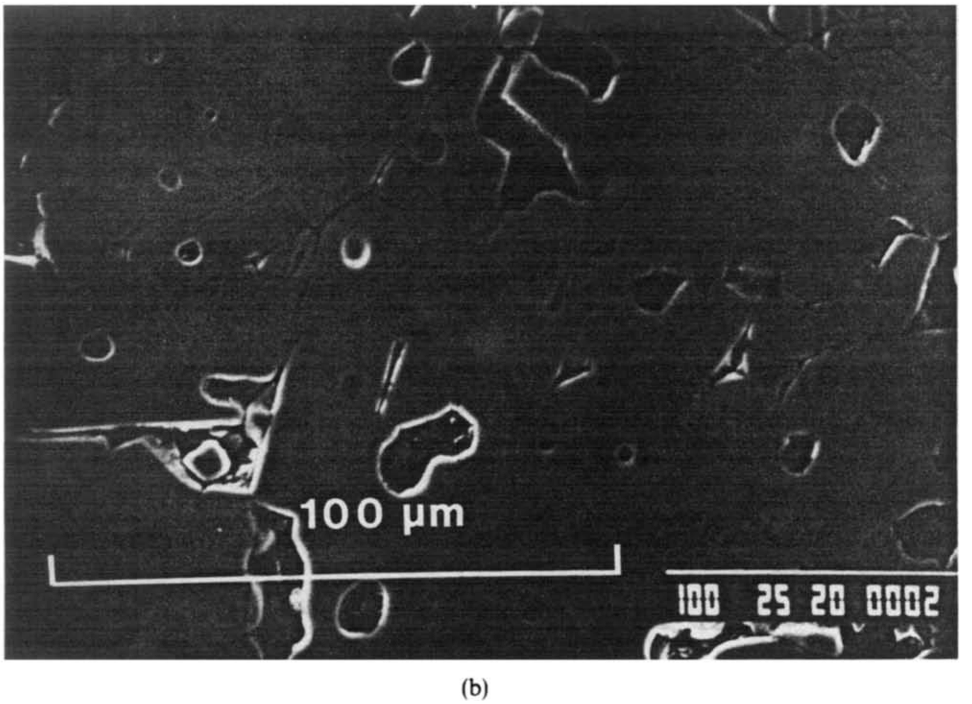
Fig. 1. Critical current density measured at 77 K in 'zero' field versus sintering time of polycrystalline $YBa_2Cu_3O_{7-\delta}$ (●) Samples annealed in air (□) Samples reannealed in oxygen at 500°C The measured grain sizes are also indicated

Table 1. Density, grain size and room temperature resistivity measurements for $YBa_2Cu_3O_{7-\delta}$ sintered at 975°C with different durations

Sintering time (h)	*Density (%)*	*Grain size (μm)*	*Resistivity at 300 K (mΩ cm)*	
			Annealed in Air	*Reannealed in O_2*
10	86	7	1 0	0 9
20	90	8	1 0	0 9
30	90	11	0 9	0 8
45	90	13	0 8	0 9
60	90	15	1 3	1 3–4 8



(a)



(b)

Fig. 2. Micrographs of $YBa_2Cu_3O_{7-\delta}$ sintered for (a) 20 h and (b) 60 h

has occurred This yields a geometrical change on the microscopic scale in the sample such that there is a reduction in the effective current-carrying cross section The presence of microcracks would also facilitate the movement of oxygen through the ceramic during annealing Consequently, reannealing in oxygen no longer increases the oxygen content

In order to confirm this hypothesis ultrasonic non-destructive tests were made on two samples (discs of 10 mm in diameter and 3 mm thick), one sintered for 20 h and the other for 60 h The velocity v_L and the attenuation α_L of a 20 MHz longitudinal ultrasonic wave were measured using an immersion pulse-echo technique For a microcracked ceramic, a decrease in v_L and an increase in α_L are expected as discussed elsewhere [7] Whereas the sample sintered for 20 h did not exhibit any propagation difficulties, there was such an increase in α_L for the sample sintered for 60 h that no echo was observed even at a lower frequency of 5 MHz, indicating considerable microcracking Furthermore, Fig. 2 shows that this microcracking occurs mainly along the grain boundaries

The origin of these microcracks can be sought in terms of anisotropic volume changes of the grains during cooling from the sintering temperature giving rise to internal stresses Such an effect due to anisotropic thermal expansion is well known in single phase polycrystalline ceramics and depends on the difference of thermal expansion coefficients along the crystal axes and on the grain size [8] In this case the microcracks follow the grain boundaries as can be observed in Fig 2. $YBa_2Cu_3O_{7-\delta}$ exhibits anisotropic thermal expansion However, another source of microcracking may be significant due to oxygen uptake associated with the tetragonal to orthorhombic phase transformation which results in anisotropic lattice parameter changes. For a change in oxygen content at 500°C from $7-\delta=6{\cdot}37$ to $7-\delta=6{\cdot}92$ the lattice parameters *a*, *b* and *c* change by $\Delta a=-0{\cdot}98\%$, $\Delta b=+0{\cdot}49\%$, $\Delta c=-0{\cdot}53\%$ [9]

Recent work by Shaw *et al* [10] reports an onset of microcracking in polycrystalline $YBa_2Cu_3O_{7-\delta}$ for grain sizes of 1–2 μm Microcracking is also used by Chiang *et al* [11] to explain a decrease in j_c between $YBa_2Cu_3O_{7-\delta}$ with a grain size of 3 μm and with a grain size of 10 μm. It can be noted in both cases that higher densities were involved (93, 95–100% respectively) An important question is whether a number of microcracks can be tolerated in the ceramic before significant effect on the electrical response. The electrical data described in the present paper indicate that at a grain size of approximately 15 μm, microcracks cause a pronounced decrease in the critical current measured for these particular samples

4 Conclusions

Microcracks occur in bulk ceramic $YBa_2Cu_3O_{7-\delta}$ when a critical grain size is exceeded due to anisotropic volume changes on cooling from the sintering temperature They reduce the effective current carrying cross section of the material resulting in lower values of j_c Further experiments, in particular the measurement of the ultrasonic parameters during cooling, are proposed to study the dependence between the temperature at which microcracking occurs and the grain size in order to obtain a better understanding of the origin of microcracks in these materials.

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