Journal of Alloys and Compounds, 189 (1992) L23–L26
JALCOM 400

Letter

Centimetre-size platelets grown from partially melted bulk $YBa_2Cu_3O_{7-\delta}$

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(Received March 30, 1992; in final form June 22, 1992)

Abstract

A single-step partial melting procedure without temperature gradient on the sample was developed. The $YBa_2Cu_3O_{7-\delta}$ platelets can be grown with their *a–b* planes almost parallel in the centimetre range. Morphological observations of regularly oriented macrospirals on the as-grown (001) surface suggest a screw dislocation growth mechanism along the *c* axis of the platelets.

1. Introduction

Partial melting procedures are the only proven techniques potentially able to solve the two main problems in applications of bulk high-T_c superconductors: the weak links between the grains and the flux-pinning capability [1]. We reported previously [2, 3] the results achieved with our single-step partial melting procedure: we obtained polycrystalline samples of $YBa_2Cu_3O_{7-\delta}$ with grains grown in the millimetre size range and typical dimensions 2×2 mm^2 cross-sectional area, even if in one sample a grain of length 6 mm and width 3 mm (the whole sample width) was seen. The grains were made of platelets almost parallel to each other with low-angle grain boundaries. Within every grain the *c* axes for all the platelets were almost parallel. Between different grains the platelets met at high-angle boundaries, which, in the view of Dimos *et al.* [4], is the most serious drawback for current transport. In addition, strong flux-pinning was estimated from the hysteresis of the levitation force, and a.c. magnetic susceptibility measurements revealed a better diamagnetic signal in comparison with precursor bars. Here we show an improved procedure, again without application of a temperature gradient on the sample, by which the platelets can grow in the centimetre size range. We also report experimental evidence which suggests a screw dislocation growth mechanism along the *c* axis similar to that observed in epitaxially grown thin films and single crystals grown using the flux method.

2. Experimental details

$YBa_2Cu_3O_{7-\delta}$ was obtained by mixing and calcining CuO, $BaCO_3$ (both purified to better than 99.9% in our laboratory) and Y_2O_3 (Rhône–Poulenc, 99.99%) in air at 900 °C. A cold isostatically pressed bar of dimensions $18\times18\times56$ mm^3 was prepared and fired. Details of the procedure were given previously [3]. By cutting the $YBa_2Cu_3O_{6.9}$ bar lubricated with organic solvents smaller precursor bars of dimensions $3\times4\times56$ mm^3 were finally obtained.

Some precursor bars were placed vertically on an alumina crucible and underwent a partial melting treatment in a muffle furnace without applying a temperature gradient on the sample. The specimens were heated rapidly in flowing air to 1080 °C, in the semisolid region where $YBa_2Cu_3O_{7-\delta}$ transforms into Y_2BaCuO_5 and a Ba–Cu-rich liquid. They were held at this temperature for some minutes, cooled quickly to a few degrees above the peritectic solidification temperature (1015 °C) [5] and cooled extremely slowly (at 0.5 K h^{-1}) to approximately 6 °C below. They were then cooled to 900 °C (at 1 K h^{-1}) and extensively reoxygenated *in situ* while cooled to room temperature. The temperature stability of the furnace was within 1 K.

Characterization was performed by the following procedures: (a) oxygen stoichiometry was determined by X-ray diffraction, putting the experimental lattice parameters in literature equation [6]; (b) morphological observations were made by optical microscopy and scanning electron microscopy (SEM), both instruments being connected to an image analyser; semiquantitative determinations were made by X-ray energy-dispersive analysis (EDXA); (c) a.c. magnetic susceptibility measurements were made on zero-field-cooled samples of dimensions $1.0\times3.5\times12$ mm^3 in the range 77–97 K, with applied magnetic fields of 1 mT and 2 mT; (d) the superconducting transition temperature was measured on the same samples in the same range of temperatures by a conventional four-probe technique.

3. Results and discussion

Partial melting procedures offer the advantage of keeping the original dimensions of the samples if care

0925-8388/92/$5.00

is taken to control the formation of excessive amounts of liquid phase. In addition, severe complications to the furnace are unnecessary if a temperature gradient can be avoided. The basic idea followed in the present work was that, on the basis of the mechanism involved for nucleation and growth of the platelets (see later for discussion), a reduction in the cooling rate to 0.5 K h^{-1} near the peritectic solidification temperature would result in growth of the platelets to larger dimensions. The slow cooling (at 1 K h^{-1}) is afterwards prolonged down to 900 °C, thus giving enough time for growth along the *a–b* planes and also for coarsening of the platelets along the *c*-axis. The remainder of the procedure was unchanged, since the oxygenation of the specimens and the stress relief was already found satisfactory in our previous work [2]. An optical micrograph of a part of a partially melted sample with a grain grown for a length of 12 mm and for a width of 3 mm is shown in Fig. 1(a).

In the remainder of the sample, grains of dimensions 3.5×3.5 mm^2 were seen. Basically, a length of almost 20 mm of sample consists of three grains. The microstructure control, although improved in comparison with previous results, is as yet far from ideal. Small particles of 2-1-1 and CuO phases remain after solidification within the grains, surrounded by the platelets which nonetheless remain parallel. Their percentage area was estimated to be 13–14% of the total and an equivalent median diameter of 20 μm was measured with an image analyser. Some areas with simultaneous occurrence of Y_2BaCuO_5, CuO and $BaCuO_2$ are clearly visible and are associated with a change of orientation of the grains. On the contrary, other areas are within a grain and the platelets are locally disturbed but keep their orientation over the long range. The atomic ratio Y:Ba:Cu:Al of the platelets was measured at several points by EDXA and the mean value was 1.17:2.02:2.79:0.02. The lattice parameters of the high-T_c phase were: $a = 3.832$ Å, $b = 3.885$ Å, $c = 11.677$ Å, with a slight shift towards a tetragonal structure. This could be due to the presence of aluminium which partially substitutes the chain copper atoms increasing the cross-linking of Cu–O chains, as reported in the literature [7], but the role of excess yttrium in our samples has yet to be clarified. In this situation the determination of the oxygen content, as made on precursor bars, is not possible. The critical temperature was 92 K (T_c onset) and the $T_c(R=0)$ was 89.5 K, measured using the four-probe technique. The normal state resistivity is considerably higher than that of precursor bars. A broadening of the transition was also estimated from a.c. susceptibility measurements.

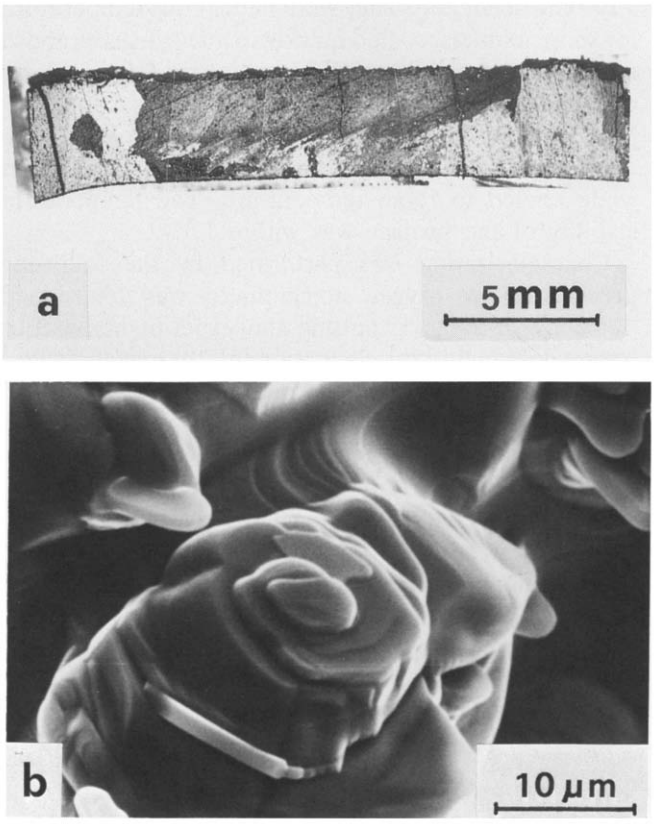
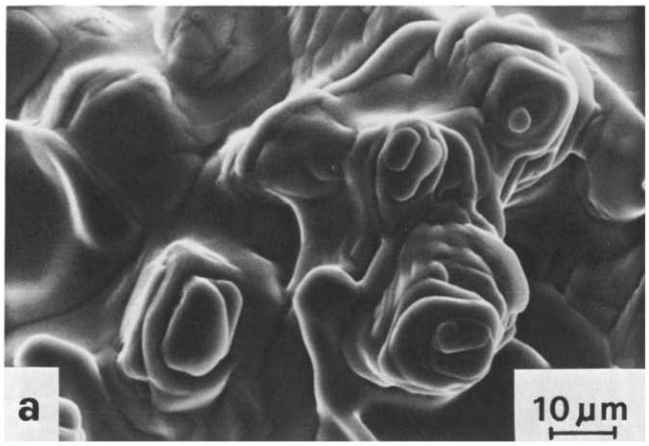


Fig. 1(a). Optical micrograph of the polished surface of a partially melted sample; (b) scanning electron micrograph of a macrospiral with helicoidal path.

Hepp *et al.* [8] outlined a fast growth mechanism along *a–b* planes limited by the liquid diffusion rate and a slow growth along the *c* axis limited by the surface nucleation rate. We agree with the former mechanism for the growth along the *a* and *b* directions, but our SEM observations on the as-grown (001) surface of partially melted samples (Figs. 1(b) and 2(a)) suggest that the growth along the *c* axis follows the same screw dislocation growth mechanism found either in epitaxially grown thin films or in single crystals [9, 10].

We find square and rectangular steps on the top of the "hills" and curved steps on the bottom. The distribution of squares and rectangles is not random but follows the two perpendicular directions reported in Fig. 2(b). On the basis of the periodic bond chain (PBC) directions theory [11], the directions are related to the *a* and *b* axes of the $YBa_2Cu_3O_{7-\delta}$ lattice. Sun *et al.* [10] found regular square figures in macrospirals having a relatively large step. The presence of rectangles in our samples may be explained by the existence of second phase particles such as Y_2BaCuO_5 or CuO. The spiral spacing is almost constant (3–5 μm), but there is a lack of regularity, probably associated with a fine dispersion of second phase particles and also with the limited amount of liquid in partially melted bars. The growth of the platelet around these particles might introduce dislocations by a mechanism [12] including a slight bending or twisting of the layers, caused by



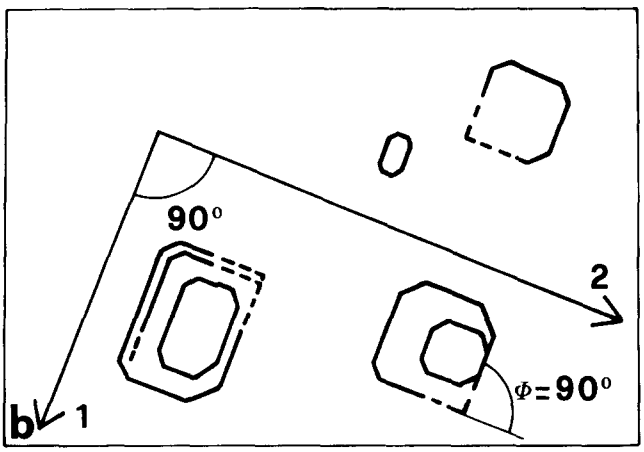
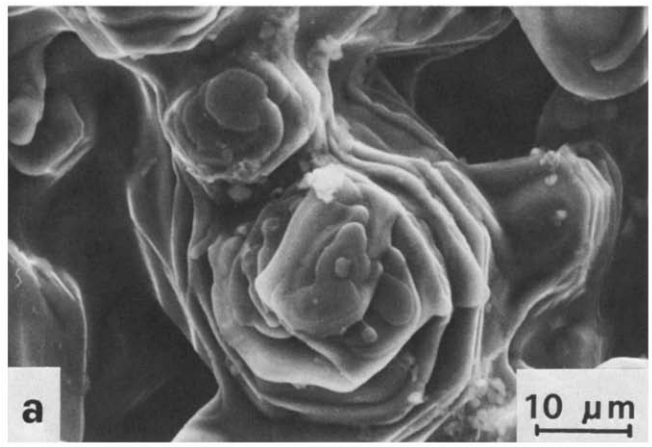


Fig. 2(a). Scanning electron micrograph of the (001) surface of a partially melted sample; (b) orientation of square and rectangular steps.



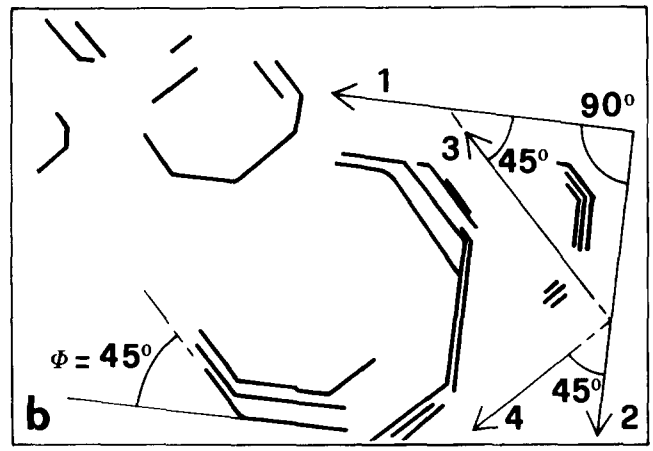


Fig. 3(a). Scanning electron micrograph of an octagonal macrospiral; (b) orientation of the steps.

thermal or concentration gradients or convection currents. These new dislocations might start the growth of additional spirals which tend to distort those already in existence. In Fig. 3(a), octagonal steps are shown.

As in Fig. 2(a), we observe a similar transition from circular (bottom) to octagonal (centre) steps. In Fig. 3(b) we show that in all the cases the edges follow a regular pattern related to the strongest bond directions (perpendicular) and the next strongest PBC directions (45°). The transitions in the steps, circular–square (or rectangular) and circular–octagonal, follow well the sequence predicted by Sun *et al.* [10] on the basis of the Jackson equation [13]:

$$\alpha = \xi L / kT_E$$

where ξ is related to the crystallographic anisotropy, L is the latent heat of melting, k is the Boltzmann constant and T_E is the absolute equilibrium temperature between solid and liquid. α is related to the roughness of the step. With high α (for lower temperatures) the steps are smooth and they cannot originate circular steps since they cannot advance independently of the crystallographic directions. Our experimental conditions approach true thermodynamic equilibrium. The growth temperature is different for different points of the growing spiral. The more elevated parts become solid regions once the temperature has decreased. The lower the temperature the higher the external angle of the polygonal step (angle Φ in Fig. 2(b) or 3(b)).

The model of screw dislocation growth predicts an increase in the fraction of preferred growth sites with undercooling and of the growth rate with the square of the undercooling [14]. This may explain why reducing the cooling speed, as we did, helps the growth of good quality partially melted samples with increasingly large grain dimensions.

In conclusion, our new partial melting procedure enables the number of grains to be reduced and as a consequence the high-angle grain boundaries. Interesting potential applications in the fields of permanent magnets and magnetic levitation can already be envisaged.

Acknowledgment

Thanks are due to I. Tangerini for helpful discussion, and to R. Guerriero and L. Meregalli for encouraging the work.

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