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Controlled growth of single-grain $YBa_2Cu_3O_7$ by top-seeding melt-texturing

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Abstract

A Top-seeding-melt-texturing (TSMT) process is investigated by quenching, in order to understand the growth mechanism better. A $SmBa_2Cu_3O_7$ melt-processed crystal has been used as a seed crystal for growing a large single-grain $YBa_2Cu_3O_7$ (Y-123) pellet in a Y-123/Y-211 composite with PtO_2-addition. It was found that the growth is three-dimensional with a growth ratio R_{100}/R_{001} close to 1. By comparing the seeded and un-seeded pellets, quenched at different temperatures during growth stage, their difference in nucleation temperatures were identified. This causes the appearance of a temperature window in which the growth of a large single-grain monolith can be realized. Finally, the growth front morphology was observed and the growth mechanism is discussed in terms of a highly supersaturated melt by the dissolution of Y-211 particles. © 1997 Elsevier Science B.V.

Keywords: Seeding; Melt-process; $YBa_2Cu_3O_{7-x}$; Single-grain

1. Introduction

Melt texture is considered to be an effective way to obtain highly oriented $YBa_2Cu_3O_7$ (Y-123) oxides [1]. This process is based on the peritectic recombination between Y_2BaCuO_5 (Y-211) and an yttrium deficient Ba–Cu–O liquid phase (L). The process results in a few mis-oriented grains separated by weak linked grain boundaries. Due to incomplete peritectic recombination, the Y-123 grains contain finely dispersed Y-211 particles which serve as pinning centers.

For several practical applications, such as magnetic bearing or magnetic levitation, well oriented single-grain monoliths of several centimeters in size are required, in order to achieve the best critical current density over the whole material and high levitation forces. The top-seeding melt-texturing (TSMT) process has been developed, using a powder melt process with platinum addition [2]. Single grain, high quality pellets with large levitation forces and trapped fields can be obtained by such a process [2,3]. The platinum addition has two roles: it keeps the sample from deforming in the semi-melt state; it reduces the coarsening of Y-211 particles in the liquid phase [4] by decreasing solid/L interface energy. However, the detailed grain growth mechanism of the TSMT process is so far not well understood and needs to be identified. In this work, we study the TSMT growth by quenching samples with or without seeding during the growth stage, and

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compare their growth behavior, in order to achieve a better understanding and control of the process.

2. Experimental

The raw powder materials used in this work are commercial Y-123, Y-211 and PtO_2 (all with a chemical purity higher than 99.9%). The investigated composition was prepared by a ball mixture through mixing Y-123 with a 60 at% excess of Y-211 and an addition of 0.5 at% platinum oxide. Pellets of diameters ranging from 16 mm to 36 mm were pressed at a pressure of 300 MPa. The crystals used for seeds are extracted from melt-textured $SmBa_2Cu_3O_{7-x}$, which is a suitable seed because it has almost the same lattice parameter in the (001) plane but possesses a higher decomposition temperature (1060°C for Sm-123 in stead of 1005°C for Y-123 [5]). The preparation condition of melt-textured Sm-123 is similar to the one noted in Ref. [2]. Typical sizes of these crystals are 3 mm × 3 mm × 2 mm. For the TSMT process, a Sm-123 seed was placed on the top surface of the pellets with the ab-plane of the seed in contact with the sample surface. Once they were assembled, they were placed into a box furnace which was then rapidly heated to 1050°C. After heating for several hours, the furnace was cooled continuously at a constant cooling rate of 2 to 0.5°C/h. For the whole thermal cycle, the slow cooling was maintained to about 930°C and then it changed to furnace cooling. For the study of the growth mechanism, quenching was performed during slow cooling at different temperatures below the peritectic recombination temperature, by pulling the samples out of the furnace. Each time, a pair of seeded and un-seeded samples were quenched together. The morphology of the growth front and microstructure were investigated by SEM (Philips XL30), optical microscopy (Olympus) and four circle X-ray diffractometry (Philips X-pert).

3. Results and discussion

Quenching was performed on pellets which were slowly cooled from 1050°C at a constant rate of 1°C/h. Fig. 1a and b show surface growth morphology of seeded and un-seeded pellets, quenched from 1000°C. We see that at this temperature none of them has begun to nucleate, even in the presence of the seed. When the quenching temperature was further decreased to 983°C, as shown in Fig. 1c, we see that for the seeded sample, a large square-faceted grain has formed. This face was confirmed to be of (001) planes by X-ray four circle diffraction analysis. On the other hand, on the un-seeded pellet no 123 crystals have formed on the surface (Fig. 1d). Further examination on the vertically cut surface reveals no formation of the 123 phase inside the pellet.

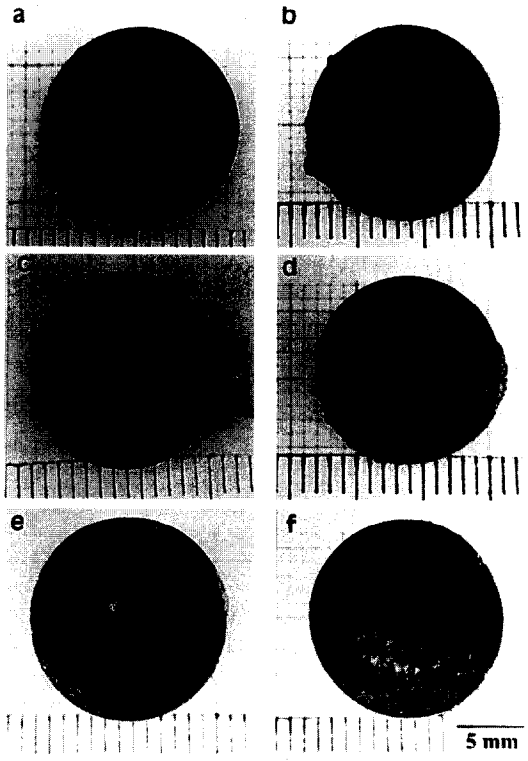

Fig. 1. The growth morphology on the top-surface of the pellets quenched from different temperatures during growth. (a) seeded, 1000°C, (b) un-seeded, 1000°C, (c) seeded, 983°C, (d) un-seeded, 983°C, (e) seeded, 960°C, (f) un-seeded, 960°C. The scale indicated on the photo (f) is used also for other photos.

At a still lower quenching temperature of 960°C (Fig. 1e), we see that the growth was stopped by the periphery of pellet, while on the un-seeded pellet, two nucleated grains have formed on the surface (Fig. 1f).

The above results indicate that the use of the seed is to stabilize a inhomogeneous nucleation center and

to promote the growth of single grain during any homogeneous nucleation is still unstable. Such a feature can be explained with the general phase transformation theory. In the case of inhomogeneous nucleation, the expression of the nucleation barrier in terms of energy ΔF^* can be written as [6]:

$$\Delta F^* = \frac{16\pi\sigma^3}{3(\Delta F_v)^2} f(\theta)$$

where

$$f(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}$$

and σ is the interfacial energy between the nucleated phase and the melt, ΔF_v is the difference in the free energy before and after phase transformation, which is proportional to the undercooling ΔT, θ is a contact angle between the nucleus, the substrate and the liquid. For a given ΔT, in the case of seeding, the seed crystal introduces a contact angle and leads to $|f(\theta)| < 1$. For an homogeneous nucleation, $\theta = 0$ and $f(\theta) = 1$, so ΔF^* is always larger. Then the nucleation rate decreases since it is proportional to $\exp(-\Delta F^*/kT)$. So the smaller the contact angle, the higher the nucleation temperature at the seeding surface. Our quenching experiments show that it is about 10°C higher than a homogeneous nucleation temperature.

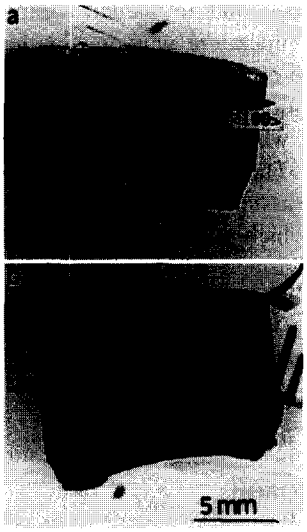

Fig. 2. The growth morphology from the {100} planes cut for the seeded samples quenched from (a) 983°C and (b) 960°C, respectively. The scale indicated for (a) is also used for (b).

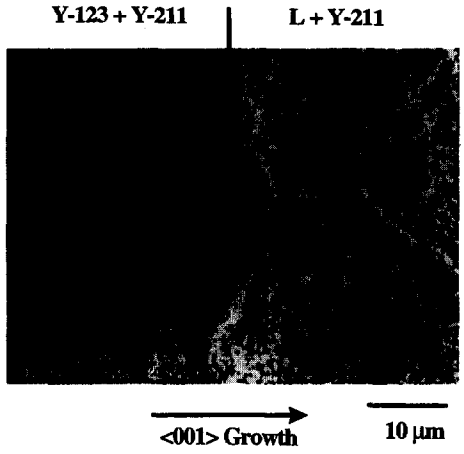

Fig. 3. The microscopic growth front of the (001) face in Fig. 2a.

In order to confirm the growth of other crystal faces, we cut the sample vertically to the top surface of the pellets and observed the polished section which is parallel to the (100) plane of the Y-123 grain. Such surfaces are shown in Fig. 2a and b, corresponding to the samples of Fig. 1c and e, respectively. X-ray four circle diffraction analysis of the $\langle 100 \rangle$ pole on these surfaces shows the single-grain nature of the Y-123 crystal. From Fig. 2a, we see that the growth front propagates in both horizontal and vertical direction and this indicates that TSMT growth corresponds to a three dimensional growth since the growth rates R of the $\langle 100 \rangle$ and $\langle 001 \rangle$ directions are quite close, with $R_{100}/R_{001} = 1.2$.

In Fig. 2b, we can see that in spite of the single-grain growth, two other domains were formed. This signifies that other nucleation from the melt has occurred. Further looking on the un-seeded sample of Fig. 1f, where two grains were formed on the top surface, we concluded that at this temperature the homogeneous nucleation is becoming stable.

In Fig. 3 we show a (001) face growth front. On the solidified Y-123 part, Y-211 particles are embedded as a consequence of an incomplete peritectic reaction. The other part contains the liquid phase with fine dispersion of the Y-211 phase. The process and mechanism of melt-texturing can be referred to

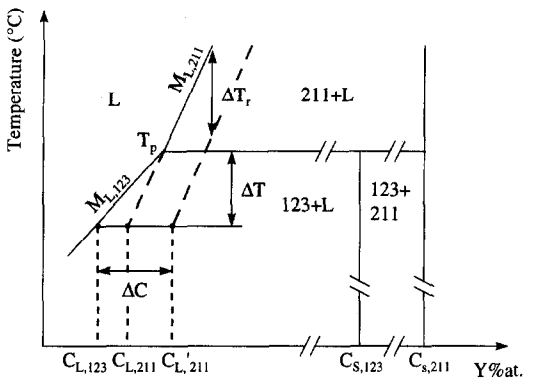

Fig. 4. A schematic phase diagram of the system Y123–Y211–$Ba_xCu_yO_z$, showing the metastable peritectic reaction and Y supersaturation.

the pseudo-ternary schematic phase diagram as shown in Fig. 4. The peritectic recombination takes place at a temperature cooled below T_p, due to constitutional undercooling ΔT [7], as indicated by the dashed line extended from the Y-211 liquidus, thus the system is unstable. The supersaturation of the liquid, which is the driving force for crystal growth, is considered to be provided by two undercoolings (Fig. 4): the first (ΔT) is due to the constitutional undercooling, the second (ΔT_r) is due to the effect of curvature of the Y-211 particles according to the Gibbs–Thomson relation, the total supersaturation ΔC can be expressed as:

$$\Delta C = (C_{L,211} - C_{L,123}) + (C'_{L,211} - C_{L,211})$$

$$= \Delta T \frac{m_{L,211} - m_{L,123}}{m_{L,123} m_{L,211}} + \frac{2\Gamma}{r} \frac{1}{m_{L,211}}$$

where the Γ is the Gibbs–Thomson coefficient, r the radius of the Y-211 particle, $m_{L,123}$ and $m_{L,211}$ are the slopes of the liquidus of Y-123 and Y-211, respectively. In order to decrease the nucleation probability, a small ΔT is suitable, therefore the main driving force is the supersaturation due to the Y-211 curvature effect.

In order to recompensate $C_{L,211}$ to $C_{L,123}$, to achieve equilibrium, Y-123 must precipitate in liquid and nucleation takes place. This is quite favorable for the sympathetic nucleation-growth model [8] which is known as the mechanism of (001) face growth in the melt process of Y-123. In this model, the growth can occur only after a two dimensional nucleation on the existing (001) face. Once nucleated, the nucleus assumes the orientation of the newly formed grain and the growth spreads through ab-direction. Once the supersaturation is recompensated, new supersaturation will restore as the growth front advances. This process repeats and allows the bulk single-grain growth.

One of the remarkable results obtained in this work concerns the very high c-direction growth velocity comparing to the case of single crystal growth using the flux method. Because of the low supersaturation related to the low yttrium solubility in the melt, about 1 at% (cf. Ref. [5]), the Y-123 single crystals grow at a very small velocity, typically about 20 μm/h in the c-direction. While in our case, we deal with a highly metastable melt in which finely dispersed Y-211 (Fig. 3) causes a high supersaturation, leading to an enhanced yttrium solubility up to more than 10 at% [9]. Accordingly high (001) growth velocity (about 400 μm/h in the present work) can be obtained.

4. Conclusion

This work shows, through a comparative study between seeded and un-seeded samples, the existence of a temperature window for the TSMT process. The role of the seed is to stabilize the heterogeneous nucleation at the surface of the seed within this window while any homogeneous nucleation is still unstable. The subsequent growth with high (001) velocity is assumed by sympathetic nucleation-growth for which an highly supersaturation melt is necessary. Through careful control of the cooling rate in the well defined temperature window, we are able to produce large single-grain Y-123 of a diameter up to 30 with a growth ratio of R_{100}/R_{001}.

Acknowledgements

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