Entrapment of elongated and crystallographically aligned pores in \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) melt-textured with \(\text{BaCeO}_3\) addition

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(Received 30 March 1998; accepted 9 December 1998)

Compared to entrapped spherical pores in \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) (123) crystals melt-textured without additives, the pores entrapped within 123 crystals melt-textured with 5 wt% \(\text{BaCeO}_3\) are elongated and aligned parallel to (100), (010), and (001) growth planes of the 123 crystals. The front side of the pores that meets first the growth front of the 123 crystal is faceted but the backside is wavy. Many \(\text{BaCeO}_3\) particles are segregated at the wavy surface. The crystallographic alignment of the elongated pores and the segregation of \(\text{BaCeO}_3\) particles are discussed in terms of the contact angle of the pores on the growth front and interfacial energy relationships between the related phases.

I. INTRODUCTION

Various types of microstructural inhomogeneities in terms of second phase distribution have been observed in melt-textured \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) (123) ceramic superconductors.\(^{1-10}\) They are exemplified by \(\text{YBa}_2\text{Cu}_3\text{O}_7\) (211) segregation along the diagonal planes of a 123 crystal (x-like tracks),\(^{1,3}\) planar 211 free regions of a trapezoid pair along a [001] direction of the 123 crystal,\(^{3,4,8}\) and spherical 211 free regions and spherical pores.\(^{5,10}\) The 211 tracks appeared frequently in stoichiometric 123 systems, while the planar 211 free regions in 211 excess systems. The formation of 211 tracks and planar 211 free regions was explained in terms of an interfacial energy relationship among 123, 211, and \(\text{Ba-Cu-O}\) liquid phases.\(^{3,8}\) In contrast, the formation of the spherical 211 free region was attributed to the formation of spherical pores due to gas evolution during incongruent melting and subsequent liquid filling into the pores.\(^{5,10}\) During the peritectic reaction to form 123 crystals, unfilled pores were trapped within growing 123 crystals and some liquid pockets were converted into spherical 123 phase regions containing only a few 211 particles.\(^{9,10}\)

Recently, we observed another type of microstructural inhomogeneity in 123 samples melt-textured with 5 wt% \(\text{BaCeO}_3\) addition. The shape of pores trapped within a 123 crystal was elongated, in contrast to entrapped spherical pores observed in undoped 123 samples. Moreover, they have an orientation relationship with the 123 crystal. In this communication, we report the microstructural characteristics of the elongated pores and discuss their formation mechanism in terms of interfacial energy relationships between related phases.

II. EXPERIMENTAL RESULTS

Figures 1(a) and 1(b), respectively, show the microstructures of (211 + liquid) region in a 123 sample without additives held at 1050 °C for 30 min and then quenched in liquid nitrogen, and a 123 region in another 123 sample melt-textured without additives from 1050 to 980 °C at 3 K/h. It is seen in Fig. 1(a) that many spherical pores are present in a mixture of 211 and a liquid phase. A spherical shape of pores in liquid implies the presence of entrapped gases within them.\(^{11}\) During extended peritectic reaction processing, small pores are filled with liquid by diffusion-out of gases from the pores, while the remaining unfilled pores are trapped within the solidifying 123 crystals. As can be seen in Fig. 1(b), the spherical pores of a few tens of microns are randomly distributed within the 123 crystals, similar to their original shape in the liquid phase.

Figure 2(a) shows the microstructure of the melt-textured 123 with 5 wt% \(\text{BaCeO}_3\) addition. Compared to the spherical pores in the undoped 123 sample, the pores trapped in this sample are elongated. The pores in 123 crystal marked as “A” are elongated perpendicular to the microcracks formed on an a-b plane of the crystal but the pores in crystal marked as “B” are parallel to the microcracks. This result indicates that the pores have an orientation relationship with the 123 crystal. Careful observation of the pores reveals that they are elongated and parallel to (100), (010), and (001) planes, the growth planes of the 123 crystal [see Fig. 2(b)]. Another characteristic feature of the entrapped pores is that one side of the pores is always faceted while the other is wavy. Few inclusion particles are present at the faceted surfaces but many small \(\text{BaCeO}_3\) particles and a
FIG. 1. Microstructures of 123 samples without additives: (a) the polished and etched surface of the sample held at 1050 °C for 30 min and then quenched in liquid nitrogen, and (b) fracture surface of the sample melt-textured from 1050 to 980 °C at 3 K/h.

few large 211 particles are present at the wavy surfaces [Fig. 2(c)].

III. DISCUSSION

Let us now discuss the cause for the formation of pores with different shapes within 123 crystals melt-textured with and without BaCeO$_3$ addition. Both in the undoped and the BaCeO$_3$-added samples, the pores in liquid are spherical. But when they come into contact with a solidifying 123 crystal, their shape should change with relative values of interfacial energies among three phases: 123, liquid (Ba$_2$Cu$_3$O$_7$), and gas (oxygen), as schematically shown in Fig. 3. When the solid/vapor interfacial energy $\gamma_{SV}$ is larger than the sum of the liquid/vapor and solid/liquid interfacial energies ($\gamma_{LV}$ and $\gamma_{SL}$), the pores will tend to be pushed by the growing 123 crystal due to the presence of a liquid film between the 123 front and the pores. In contrast, when $\gamma_{SV}$ is smaller than the sum of $\gamma_{LV}$ and $\gamma_{SL}$, the pore will be attached to the 123 crystal and easily trapped within it. Under this circumstance, the pore shape must be determined by the contact angle $\theta$ of the pore at the surface of the growing 123 crystal, as shown in Fig. 3(b), satisfying the interfacial energy relationship,

$$\gamma_{LV} \cos \theta + \gamma_{SV} = \gamma_{SL}. \tag{1}$$

When $\theta$ is large [Fig. 3(c)], the shape of entrapped pores will be almost spherical, similar to that observed in Fig. 1(b); but when $\theta$ is small [Fig. 4(d)], it will be a thin plate similar to that observed in Fig. 2. It appears that the pore contact angle on the growth planes ([100], [010], and [001]) of 123 crystals decreases considerably with addition of 5 wt% BaCeO$_3$. The relative values of the interfacial energies $\gamma_{LV}$, $\gamma_{SV}$, and $\gamma_{SL}$ should change with BaCeO$_3$ addition. Since a 123 crystal grows with faceted {100} planes, a pore will spread to form a lens-like void, as schematically shown in Fig. 3(d), when it comes in contact with the crystal. With the crystal growth, the lens-like pore will be trapped, maintaining more and less its shape. The result of the entrapment may then be a faceted front surface and wavy rounded back surface of the pore, as observed in Fig. 2.

Preferential segregation of solute atoms on specific crystallographic planes of a crystal was well documented$^{12-14}$: for example, strong segregation of calcium on {1010} prism plane of Al$_2$O$_3$. In the present investigation, the 123 crystal with 5 wt% BaCeO$_3$ addition

FIG. 2. Microstructures of a 123 sample melt-textured with 5 wt% BaCeO$_3$ addition: (a) 123 crystals containing elongated pores (the dark regions), (b) pores elongated perpendicular to the growth directions of 123 crystals, and (c) faceted front surface containing a few BaCeO$_3$ particles and wavy back surface containing many BaCeO$_3$ particles.
appears to be a case of preferential segregation. Cerium is thought to be segregated preferentially on the growth planes of 123 crystals and changes significantly their interfacial energy, resulting in considerable change in pore contact angle.

The effect of the added BaCeO$_3$ particles was not limited to the pore shape change. The particles themselves were trapped within growing 123 crystals to form linear tracks parallel to (100), (010), and (001) growth planes of the 123 crystal, as shown in Fig. 4. The formation of BaCeO$_3$ linear tracks in 123 crystals may be explained by pushing, agglomeration, and trapping of the particles as in previous investigations. With the growth of {100} fronts of a 123 crystal, the BaCeO$_3$ particles present ahead of the crystal are thought to be pushed because of their small size. The particles will then be agglomerated in front of the growing crystal, acting as a large particle. In directionally solidified Al–Ni–SiC alloys, SiC agglomerates were trapped within the advancing solid interface, while individual SiC particles were pushed away. Similarly, the agglomerates of BaCeO$_3$ particles may be trapped within the 123 crystal when the size is larger than the critical size of the particle–pushing criteria, forming BaCeO$_3$ linear tracks, as shown in Fig. 4.

The segregation of BaCeO$_3$ particles at the backside wavy surface of entrapped pores in Figs. 2(b) and 2(c) is another characteristic of nonuniform distribution of the particles. This particle segregation may be a result of pushing, agglomeration, and trapping of the particles. In this case, however, possible changes in relative interfacial energies among solid, liquid, and gas are thought to be more significant. If BaCeO$_3$ particles are completely wetted with the liquid phase, BaCeO$_3$ particles are expected to be homogeneously dispersed in the liquid phase, as schematically shown in Fig. 5(a). In this case, the segregation of BaCeO$_3$ particles around the pores would not frequently occur. On the contrary, when the wetting angle on BaCeO$_3$ is large, BaCeO$_3$ particles are expected to be floated and always segregated at the liquid/vapor interface [Fig. 5(b)]. With the growth of a 123 crystal, the segregated BaCeO$_3$ particles will then be trapped, as shown in Fig. 2(c). It appears that the wetting angle is rather high, which results in the segregation of BaCeO$_3$ particles on the backside wavy surface of pores.

IV. CONCLUSIONS

In summary, the spherical pores formed within (211 + liquid) mixture during incongruent melting became elongated ones and aligned parallel to the growth planes of a 123 crystal when they were trapped into the 123 crystal melt-textured with 5 wt% BaCeO$_3$ addition. The frontside surface of elongated pores, the surface met first with the growing front of a 123 crystal, was faceted and the backside surface was wavy. At the backside surface, many BaCeO$_3$ particles were segregated. The
observed pore shape change and alignment were well explained in terms of the contact angle of the pores at the growth planes of a 123 crystal. It appeared that the BaCeO$_3$ addition changed considerably the relative interfacial energies among solid, liquid, and gas phases. The segregation of BaCeO$_3$ particles at backside of entrapped pores was thought to be due to poor wetting of the particles with liquid.

ACKNOWLEDGMENT

This work was supported by the Ministry of Science and Technology (MOST) of Korea.

REFERENCES


FIG. 5. Schematic of the distribution of BaCeO$_3$ particles around a contact pore for (a) complete wetting and (b) poor wetting of the particles.