Available online at www.sciencedirect.com

ScienceDirect

Journal of Crystal Growth 307 (2007) 432–439

JOURNAL OF CRYSTAL GROWTH

www.elsevier.com/locate/jcrysgro

Effect of an external electric field on the crystal growth process of YBCO superconductive oxide

Xinming Huang*, Satoshi Uda, Shinji Koh

Institute for Materials Research, Tohoku University, Sendai 980 8577, Japan

Received 23 April 2007; received in revised form 15 June 2007; accepted 20 June 2007
Communicated by R.S. Feigelson
Available online 23 June 2007

Abstract

The crystal growth process of YBCO superconductive oxide under an external electric field has been investigated by means of in situ observations and differential thermal analysis. The effects of an external electric field on the growth processes via the peritectic reaction of 123 ($YBa_2Cu_3O_{7-x}$) crystals from liquid +211 (Y_2BaCuO_5), including (1) dissolution of the 211 phase into solution, (2) transportation process of the solute, Y (Y_2O_3), in the liquid, and (3) kinetic attachment of the solute to the growth front, were analyzed in detail based on the coupling equation. An external electric field of 600 V/cm resulted in the generation of an electric double layer either at the interface between the solution and the ambient atmosphere or at the interface of the solution and the 211 grains; however, almost no electric field could be generated in the bulk liquid due to it being electrically conductive. The external electric field enhanced dissolution of the 211 gains slightly, but had almost no effective electric field operated on the transportation process of the solute, and little effect was observed on the attachment kinetics. On the other hand, the external electric field increased the Gibbs energy for the nucleation of the 123 grains, which retarded the nucleation of the 123 grains.

PACS: 81.40.Tv; 74.25.Dw; 81.10.Aj; 81.10.Dn

Keywords: A1. Crystal growth; A1. External electric field; A1. Nucleation; A1. Peritectic reaction; B1. YBCO

1. Introduction

Melt-textured processing, involving partial melting and recrystallization during cooling, is known to be an effective method for growing large-sized $YBa_2Cu_3O_{7-x}$ (1 2 3) superconducting bulk crystals. The peritectic reaction of 211 (Y_2BaCuO_5) + L(liquid) → 123, as elucidated by Dembinski et al. [1], was used for growing such 123 crystals [2]. In this reaction, the 123 crystals grow directly from the liquid upon dissolution of 211 crystals into the liquid [3]. The supersaturation required for growing 123 crystals via this peritectic reaction has been categorized into three different components based on the coupling equation [4], which was used by Mori et al. [5], namely, (1) dissolution of the 211 phase, ΔC_m; (2) transportation of the solute, ΔC_t; and (3) kinetic attachment of the solute to the growth front, ΔC_k.

Scanning tunneling microscopy was used to investigate the growth mechanism of 123 crystals, and the results indicate that the growth of surfaces of 123 crystals with different indices have different mechanisms. Single or double spirals were observed on (0 0 1) surface [6,7], whereas a source of steps existed at the edge between (1 0 0) and (0 1 0) surfaces, which resulted in numerous steps flowing on the (1 0 0) surface from the edge [8]. Many in situ observations of crystal growth of 123 crystals via the peritectic reaction have also been performed for gaining a deeper understanding of the growth process [3,9,10].

Applying an external electric field to a crystal growth system affects the crystallization process in two ways; specifically, it affects the thermodynamics of the system and the growth dynamics. The former modifies the chemical potentials of the associated phases in equilibrium,

---

*Corresponding author. Tel.: +81 22 215 2102; fax: +81 22 215 2101.
E-mail address: x.huang@imr.tohoku.ac.jp (X. Huang).

0022-0248/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2007.06.021

which could, for example, convert an incongruent-melting state into a congruent-melting state [11]. An external electric field also affects growth dynamics, such as the nucleation process and the growth kinetics. Kashchiev proposed a model to describe the effect of an external electric field on the nucleation rate, based on the supposition that the electric field is uniform before the nucleus formation and has the same uniform value at a large distance from the nucleus after its formation [12]. Isard modified Kashchiev's model by considering an external electric field generated by a system having a fixed potential at the electrodes, and showed that this modification requires an additional free energy term to the Gibbs free energy for nucleation [13].

In a system with a high-temperature conductive oxide melt, most of the applied external electric potential is consumed in the electric double layer (EDL), which is presumably generated between the melt and the metallic container, or at the interface between the melt surface and the atmosphere, or at the boundary of the melt and the crystal embryos. A huge electric field is expected at these boundaries, and we have demonstrated that an electric field as high as 10^4–10^5 V/cm can be generated at the EDL in the crystal growth of langasite ($La_3Ga_5SiO_{14}$) by applying an external electric field of 600 V/cm [14].

The influence of an external electric field on the growth dynamics of the 123 phase, including growth kinetics and nucleation process, was investigated in a previous study by us by means of in situ observations [15]. It was found that the external electric field did not affect the attachment kinetics during the growth of 123 crystals, but that the nucleation process was retarded by the additional electrostatic energy. In this study, we investigate the effects of an external electric field on the overall growth process, including the nucleation process and growth dynamics, i.e., dissolution of the 211 phase, transportation of the solute and kinetic attachment of the solute to the growth front.

2. Experimental procedure

Samples of 123 phase with a cation ratio of Y:Ba:Cu = 1:2:3 were synthesized from Y_2O_3, $BaCO_3$, and CuO powders with 4N purity via a solid-state reaction. The raw materials were mixed thoroughly and reacted in a high-purity alumina crucible in air at 850 °C for 24 h and at 900 °C for 96 h. The samples were repeatedly ground using an alumina mortar before and after each heat treatment process. X-ray diffraction analysis showed that more than 97% of the synthesized powder samples was the 123 phase. Several samples with a composition of 211 (70%) + 7BaO–18CuO (30%) were also synthesized and the same procedure was used for investigating the dissolution of the 211 phase. As shown in the pseudo-binary phase diagram along 123 to 7BaO–18CuO [1], dissolution of the 211 phase was realized using a sample having the composition indicated by the arrow of α in Fig. 1.

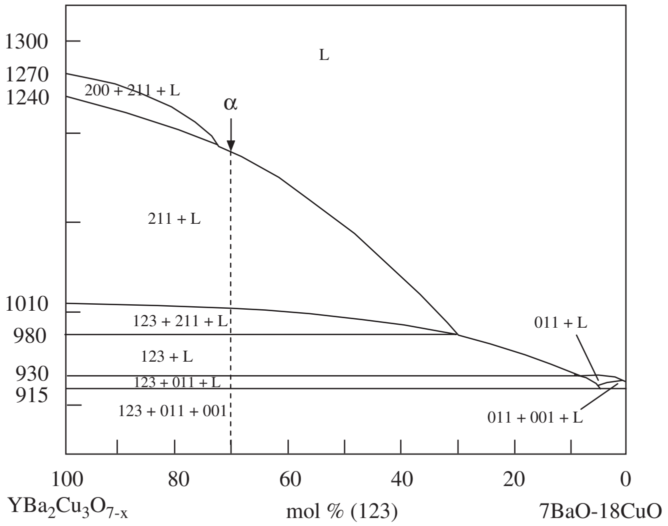

Fig. 1. A pseudo-binary phase diagram along 123 to 7BaO–18CuO. Samples with the composition indicated by the arrow of α in the pseudo-binary phase diagram were used for measuring the dissolution process of 211.

A specially designed DTA (differential thermal analysis) system was constructed in-house that enabled an external electric field to be applied to the sample (Fig. 2). For the DTA measurements, a powder sample of about 15 mg was directly charged in a high-purity alumina pan (5 mm in diameter and 2.5 mm in height). The sample was placed in the center of a vertical furnace with a chamber that was 20 mm in diameter and 35 mm in height. A pair of electrodes was positioned around the sample; it could apply AC (500 Hz) electric fields of up to 600 V/cm to the sample. The electrodes were electrically insulated by thin alumina plates that were 0.4-mm thick. It should be noted that there was no carrier injection into the sample, however, the sample was located in a potential field, and by this means electrostatic energy was applied to the sample. The dissolution of the 211 phase was examined in detail using the DTA at different heating rates while applying an external electric field. Relatively high heating rates (20–50 °C/min) were employed in order to avoid any influence of reactions occurring between the high-temperature liquid and the alumina pan.

In situ observations could also be made in the DTA system using a CCD camera and a microscope having a maximum magnification of 300. The growth of 123 crystals both with and without an external electric field was observed in situ in the temperature range of 1001–1010 °C, and the growth rate was measured at different supercoolings. A detailed experimental procedure for the in situ observations has been reported previously [15].

The temperature of the sample was measured using an R-type thermocouple (Pt-Rh-13%Pt) which was placed just below the sample, and the temperature was calibrated by measuring the melting point of Au ($T_m = 1063.4\,°C$). The error in the temperature measurement was estimated