Growth Rate of $YBa_2Cu_3O_7$ Bulk Crystals in $Y_{1.5}Ba_2Cu_3$ System with CeO_2 Addition*

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The growth rate of $Y_1Ba_2Cu_3O_x$ bulk single grain (in fact single crystal) superconductors in the system with composition $Y_{1.5}Ba_2Cu_3O_x$ and CeO_2 addition was studied in the temperature range 991–1001 °C. It is shown that the growth rate of bulk crystal is different for *a*- and *c*-growth direction. Slower measured growth rate in studied system than in pure $Y_1Ba_2Cu_3O_x$ is related to the composition shift to the three-phase field containing CuO.

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1. Introduction

$YBa_2Cu_3O_7$ (Y123) bulk high temperature superconductors represent progressive material prepared as massive single crystals (usually cylinders with maximum diameter more than 100 mm). The mostly used technology for production of this material is so-called top-seeded melt-growth (TSMG) process [1–3]. The TSMG process involves heating of the pressed $YBa_2Cu_3O_7$ powder (with addition of Y_2O_3 to form excess of Y_2BaCuO_5 particles or direct addition of Y_2BaCuO_5 powder) to a temperature above that of the peritectic decomposition (incongruent melting) of the $YBa_2Cu_3O_7$ phase [4] at $T_{p123} = 1010\,^{\circ}C$ in air. During slow cooling, the $YBa_2Cu_3O_7$ crystal grows epitaxially from the seed, located at the top surface of the cylindrical sample, from an under-cooled mixture of Y_2BaCuO_5 particles and a melt. Important point of this epitaxial growth is the requirement to find temperature window for growth of $YBa_2Cu_3O_7$ single-grain (in fact single-crystal) below the temperature of heterogeneous nucleation on the used seed (T_{HN}) and beyond the temperature of self nucleation (T_{SN}) of $YBa_2Cu_3O_7$ phase. This window is usually very narrow and also quality of grown sample depends on the position in this window and consequent crystal growth rate. Growth rate, R, of $YBa_2Cu_3O_7$ crystal nucleated on the seed is technologically important parameter for fabrication of YBCO bulks.

In this paper we show the results of experimental study of $YBa_2Cu_3O_7$ crystal growth in the $Y_{1.5}Ba_2Cu_3O_x$ system (modified melt growth process [5]) with CeO_2 addition (CeO_2 added for Y_2BaCuO_5 particle refinement). The refinement of Y_2BaCuO_5 particles by CeO_2 addition is significantly influenced by Ce dissolved in the peritectic melt, *Lp*, which can actively hinder the Y_2BaCuO_5 particle growth by the Ostwald ripening process [6]. Ce is trapped in the growing $YBa_2Cu_3O_7$ crystal in the form of $BaCeO_3$ particles [7].

2. Experimental

YBCO bulk polycrystalline samples with nominal composition $Y_{1.5}Ba_2Cu_3O_x$ with 1 wt% CeO_2 additions were prepared in air in a chamber furnace. $YBa_2Cu_3O_7$, Y_2O_3, and CeO_2 powders were mixed in appropriate amounts in a mixer for 30 min and then intensively milled for 25 min in a friction mill. We used the fraction of $YBa_2Cu_3O_7$ powder with the mean particle 30 μm. Homogenized and milled mixture of powders was uniaxially pressed into the cylindrical pellets of 20 mm in diameter. The samples were treated in a chamber furnace: heating up at the rate of 100 °C/h to 940 °C/dwell 24 h, heating up at the rate of 100 °C/h to a maximum temperature 1040 °C (30 °C over peritectic temperature, T_p), dwell time for 10 h, fast cooling to temperature 12 °C higher than temperature of isothermal grow, T_{is}, at the rate of 50 °C/h , slow cooling to isothermal hold temperature, T_{is}, with cooling rate 1 °C/h and finally cooling to room temperature with furnace. The slow cooling rate to the dwell temperature was used to equilibrate melt composition because the solubility of Y in the melt is a function of temperature [8]. The macrostructure of the sample surface was done by a stereo microscope.

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3. Results and discussion

As one part of $YBa_2Cu_3O_7$ crystal was grown during slow cooling to the T_{is}, it was necessary to grow at least two crystals with different growth time to estimate growth rate at isothermal conditions. These experiments were done for three temperatures in the temperature window for growth of $YBa_2Cu_3O_7$ single crystals: 991, 996, and 1001 °C. The example of asóh growth of $YBa_2Cu_3O_7$ crystals at different isothermal dwells is presented in Fig. 1.

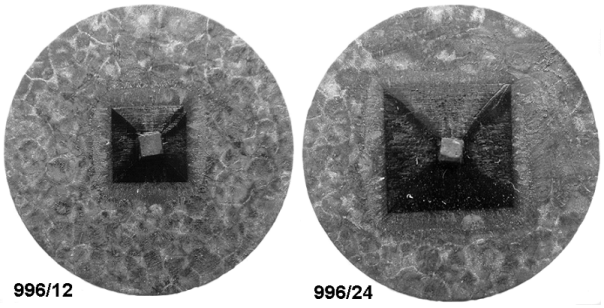

Fig. 1. Example of top surface macrographs samples grown at different temperatures/isothermal dwells.

The growth length in the a-direction was measured on the top sample surface and the growth length in the c-direction was measured on the cross-sections of the sample along the a/c-plane (Fig. 2).

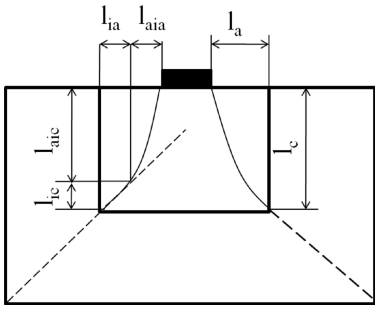

Fig. 2. Schematic presentation of idealized shape of growth sectors on the a/c-cross-section. The part of the $YBa_2Cu_3O_7$ crystal, which grew during slow cooling (l_{aia}, l_{aic} are the lengths of the crystal grown under anisothermal conditions in the a-direction and c-direction, respectively) has bended growth sector boundary due to changes in R_a/R_c ratio (R_a — growth rate in the a-direction, R_c — growth rate in the c-direction). R_a/R_c is supposed to be constant during isothermal growth.

The growth rates in the a-direction, R_a, and in the c-direction, R_c, were calculated for the middle part of the $YBa_2Cu_3O_7$ crystal grown under isothermal conditions and are plotted in Fig. 3. Both growth rates are practically linearly dependent on under-cooling, ΔT, while the growth rate in the c-direction is slightly higher. These

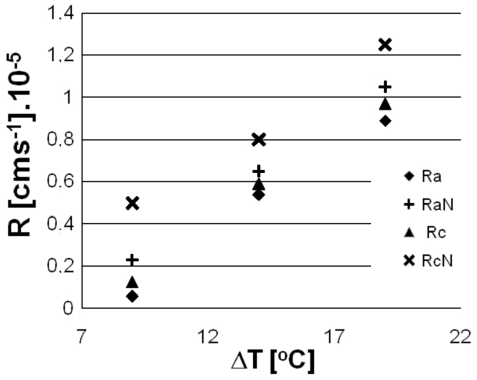

Fig. 3. Growth rate, R, in a- and c-directions versus undercooling, DT, measured for the samples with Y_2O_3 and CeO_2 additions compared with growth rate by Nakamura and Shiohara, RN [6], measured for pure $YBa_2Cu_3O_7$ system. $\Delta T = T_p - T_{is}$ (T_p is the peritectic temperature = 1010 °C, T_{is} is the temperature of isothermal growth).

data are compared with the data by Nakamura and Shiohara [9] measured for pure $YBa_2Cu_3O_7$ system. The growth rates for our samples with Y_2O_3 and CeO_2 additions are systematically lower, but dependences are similar. Extrapolation to zero growth rate suggests that the window for epitaxial growth of $YBa_2Cu_3O_7$ crystal from Sm123 seed starts at 1003 °C. The start of $YBa_2Cu_3O_7$ crystal growth at lower than peritectic temperature is obviously caused by appearance of CuO in the system when Y_2O_3 is added according to reaction

$$YBa_2Cu_3O_{7-x} + (3/2)Y_2O_3 + zO_2 = 2Y_2BaCuO_5 + 2CuO \quad (1)$$

and consequent decrease of the temperature when first $YBa_2Cu_3O_7$ starts to crystallize in the system [4].

Knowing the growth rates, the lengths of the part of $YBa_2Cu_3O_7$ crystal, which was grown at anisothermal conditions, l_{aia}, l_{aic}, (Fig. 2) were calculated (Table).

TABLE

Calculated sizes of the $YBa_2Cu_3O_7$ crystal grown during anisothermal conditions. l_{aia} is the length of the crystal grown in the a-direction, l_{aic} is the length of the crystal grown in the c-direction.

T_{is} [°C]	l_{aia} [mm]	l_{aic} [mm]
991	2.6	1.4
996	1.7	1.5
1001	0.7	1.7

The size of the $YBa_2Cu_3O_7$ crystal is higher for lower T_{is} what is caused by longer time of slow cooling period spent at higher under-cooling with higher growth rates. The size of the $YBa_2Cu_3O_7$ crystal grown at slow cooling does not represent significant portion of the $YBa_2Cu_3O_7$ crystal grown under isothermal conditions.

4. Conclusions

The YBCO bulk superconductors with composition $Y_{1.5}Ba_2Cu_3O_x$ and CeO_2 addition were grown as single crystals by TSMG process under isothermal conditions at temperatures. The growth rates in the a- and c-direction were measured and their dependence on under-cooling was shown. Extrapolation to zero growth rate suggests that the window for epitaxial growth of $YBa_2Cu_3O_7$ crystal from Sm123 seed starts at 1003 °C. The start of $YBa_2Cu_3O_7$ crystal growth at lower than peritectic temperature is obviously caused by appearance of CuO in the system when Y_2O_3 is added and consequent decrease of the temperature when first $YBa_2Cu_3O_7$ starts to crystallize in the system.

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