

# Suppression of the surface nucleation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ by $\text{CeO}_2$ coating of the top-seeded melt processed YBCO superconductors

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**Abstract**— The effect of  $\text{CeO}_2$  coating on the surface nucleation of the top-seeded melt-growth processed YBCO superconductors was studied. It was effective that the coating of Y123 compact surfaces by  $\text{CeO}_2$  powder suppressed the undesirable subsidiary  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  (Y123) nucleation during melt processing.  $\text{BaCeO}_3$  was formed in the  $\text{CeO}_2$ -coated layers, which might cause a CuO-excessive liquid at the partial melt stage of  $\text{Y}_2\text{BaCuO}_5$  (Y211) plus liquid, and thus the Y123 nucleation at the YBCO compact surfaces could be suppressed during the melt growth of Y123 grain. In addition, the  $\text{CeO}_2$  refined the Y211 particles near the compact / coating interface. While the levitation forces of the top surfaces with and without  $\text{CeO}_2$  coating were similar to each other, the levitation force of the interior of the  $\text{CeO}_2$  coated sample was higher than that of the interior of the sample without  $\text{CeO}_2$  coating, which was attributed to the suppression of subsidiary Y123 nucleation at the compact walls.

**Keywords** :  $\text{CeO}_2$  coating, surface nucleation, top-seeded melt growth process, Y-Ba-Cu-O superconductor

## 1. INTRODUCTION

The load-bearing capacity of bulk superconductors depends both on the critical current density and grain size of the superconductors. To achieve a large levitation force, it is necessary to make a single grain sample. The single grain YBCO superconductors are, in general, fabricated by the top-seeded melt growth (TSMG) process [1-7]. The TSMG process consists of placing a  $\text{SmBa}_2\text{Cu}_3\text{O}_x$  or  $\text{NdBa}_2\text{Cu}_3\text{O}_x$  single grain seed on the top surface of a YBCO compact, heating the seeded compact to a partially molten state and cooling it slowly through a peritectic temperature ( $T_p$ ). At temperatures just below  $T_p$ , single  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (Y123) nucleates at the seed and grows further toward the whole compact. To fabricate a Y123 single grain sample, the Y123 nucleation and growth at the seed should thus be carefully controlled. Referring to previous work [8], the undesirable subsidiary Y123 grains were often observed in the TSMG processed YBCO samples, which made it difficult to make a single grain YBCO superconductor.

Meignan et al. [9] suggested a way of suppressing the surface nucleation in a TSMG process, which was surface coating with  $\text{Yb}_2\text{O}_3$  powder. The basic concept of this

method is to make a melt with a lower melting point (m. p.) at the compact surfaces. If the compact surface forms the melt at lower temperature than the compact interior does, nucleation of Y123 can be suppressed at the compact surface even though the Y123 grain grows in the interior of the compact [9,10]. The peritectic melt formed in the  $\text{Yb}_2\text{O}_3 - \text{BaO} - \text{CuO}$  system has relatively lower m. p. compared with those produced in  $\text{Yb}_2\text{O}_3$  or other rare-earth metal oxides -  $\text{BaO} - \text{CuO}$  systems. That is the reason why  $\text{Yb}_2\text{O}_3$  was thus used as the surface coating medium. Shi et al. [11] showed that the CuO coating also suppressed the surface nucleation in a similar manner to the  $\text{Yb}_2\text{O}_3$  coating. It lowered the m. p. of the coated region by forming a pseudo-peritectic (p1) melt.

In this study, the effect of  $\text{CeO}_2$  coating on the surface nucleation of the TSMG-processed YBCO superconductors was investigated to find whether  $\text{CeO}_2$  can also be used as an effective coating medium like  $\text{Yb}_2\text{O}_3$  and CuO. The reaction between the  $\text{CeO}_2$  and the Y123 powder in the coated region and the additional effect on the levitation forces are reported.

## 2. EXPERIMENTS

YBCO compacts were prepared from a powder mixture of 1 mole Y123 and 0.4 mole  $\text{Y}_2\text{BaCuO}_5$  (Y211) powders ( $\text{Y}_{1.8}\text{Ba}_{2.4}\text{Cu}_{3.4}\text{O}_x$ ; Y1.8). 40 g of Y1.8 powder was pressed uniaxially in a square mold of a dimension of  $3 \times 3 \text{ cm}^2$  and then isostatically pressed in a water chamber. To understand the effect of  $\text{CeO}_2$  coating on the surface nucleation, we prepared two sets of Y1.8 compacts coated with and without  $\text{CeO}_2$  powder. One set of Y1.8 compacts was not coated, while the surfaces of another set of Y1.8 compacts except the top surface were coated with  $\text{CeO}_2$  powder, as shown in Figs. 1(a) and (b).  $\text{Sm}_{1.8}\text{Ba}_{2.4}\text{Cu}_{3.4}\text{O}_x$  ( $\text{Sm}1.8$ ) seeds were placed at the centers of the top surfaces of both compacts. The seeded compacts were placed on single crystal MgO substrates, positioned at the center of an electrical box furnace and melt-processed following the heating cycles as shown in Fig. 2. The melt-processed samples were annealed at  $500^\circ\text{C}$  for 50 h in flowing oxygen gas for the tetragonal-to-orthorhombic phase change. Magnetic levitation force of the samples was measured from the force-distance curves at 77 K (liquid nitrogen) using a Nd-B-Fe permanent magnet with a diameter of 20 mm and surface magnetic field of 4000 Gauss.

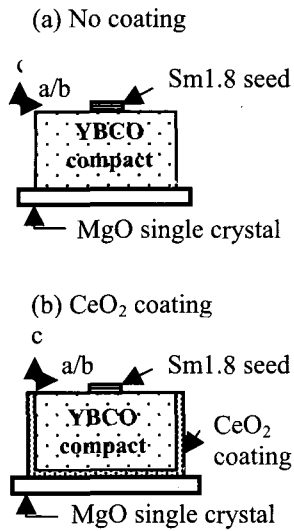
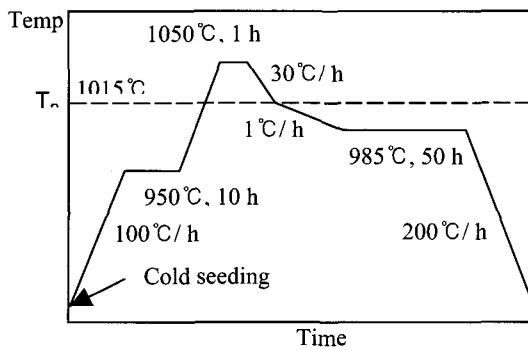


Fig. 1. Schematics of top-seeded YBCO compacts with (a) no coating and



(b) CeO<sub>2</sub> coating.

Fig. 2. Heating cycle of the melt process.

### 3. RESULTS AND DISCUSSION

Figs. 3(a) and (b) show the photos of the top surfaces of the TSMG-processed YBCO samples with and without CeO<sub>2</sub> coating, respectively. The top surface growth morphologies of both samples are similar. The rectangular shaped Y123 grains nucleated at the seeds and grew toward the whole samples. No subsidiary Y123 grain is observed in both the top surfaces.

Figs 4(a) and 4(b) are the photos of the compact walls of the samples without CeO<sub>2</sub> coating and with CeO<sub>2</sub> coating. The surface morphology of the compact wall of the sample with CeO<sub>2</sub> coating is different from that of the sample without CeO<sub>2</sub> coating. As can be seen in Fig. 4(a), several randomly grown Y123 grains are observed at the compact wall of the sample without CeO<sub>2</sub> coating. They appear to nucleate at the compact walls or from a substrate and to grow toward the compact interior. Unlike the sample without CeO<sub>2</sub> coating, no surface nucleation is observed in the sample with CeO<sub>2</sub> coating. Instead of the surface nucleation, the surfaces of sample (b) are covered with the

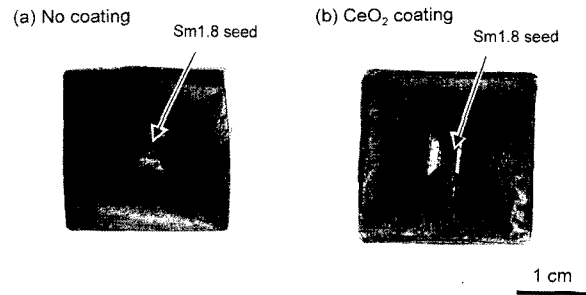


Fig. 3. Photographs of the top surface of the TSMG-processed YBCO sample with (a) no coating and (b) CeO<sub>2</sub> coating

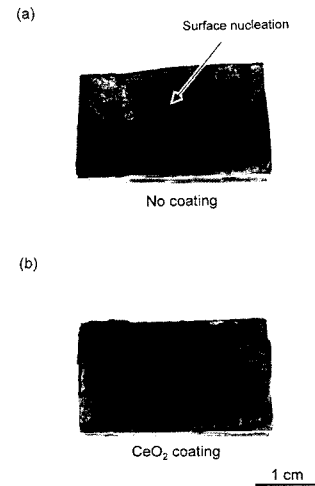


Fig. 4. Photographs of the compact walls of the TSMG-processed YBCO sample with (a) no coating and (b) CeO<sub>2</sub> coating.

compounds formed by the reaction between the CeO<sub>2</sub> and the compact surfaces.

Figs 5(a) and (b) show the force-distance (F-D) curves for the top surfaces of the TSMG-processed YBCO samples with and without CeO<sub>2</sub> coating, and cooled without a magnetic field. The curves of both samples show a hysteresis behavior with large repulsive and small attractive forces due to the high  $J_c$  of the top surfaces. The maximum levitation forces ( $F_{max}$ ) at  $d=1$  mm for samples (a) and (b) are 34 N and 37 N, respectively ( $d$  is a distance between a superconductor and a permanent magnet). The similar  $F_{max}$  values of both samples are attributed to the similar growth mode of the top surfaces as shown in Figs. 3(a) and (b).

As observed in Figs. 3 and 4, the growth mode of the top surfaces was similar, but the mode of the compact walls was different. The subsidiary nucleation at the compact wall can affect the levitation of the sample interior. To understand the effect of the subsidiary nucleation on levitation force, the top surfaces of the samples were moved by means of a diamond cutter until the sample thickness was 8 mm.

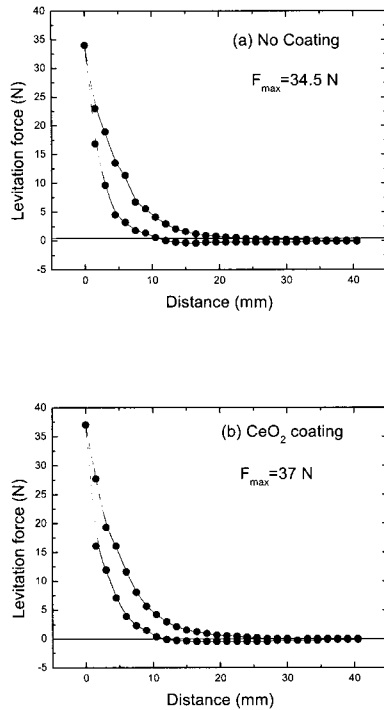


Fig. 5. Force-distance hysteresis curves of the top surface of the TSMG-processed YBCO sample with (a) no coating and (b)  $\text{CeO}_2$  coating.

Figs 6 (a) and (b) are F-D curves of the 8 mm samples with no coating and  $\text{CeO}_2$  coating, respectively. Compared to the hysteresis curves of the top surfaces of Fig. 4, the

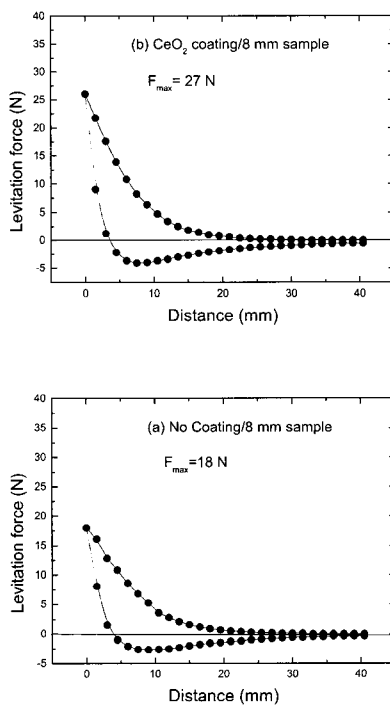


Fig. 6. Force-distance hysteresis curves of the TSMG-processed YBCO samples whose top parts were removed to a sample thickness of 8 mm : (a) no coating and (b)  $\text{CeO}_2$  coating.

levitation forces of the samples are smaller and the attractive forces are larger. When we compared the hysteresis curves of the two samples, the  $F_{\text{max}}$  of the sample with  $\text{CeO}_2$  coating is 27 N, which is much higher than 18 N of the sample without  $\text{CeO}_2$  coating. These values are, however, only 52% and 70% of the values of the original top surfaces of each sample. This is due to the smaller sample thicknesses [12]. The difference in  $F_{\text{max}}$  values is related to the surface nucleation. As observed in Fig. 4, the compact surfaces with no  $\text{CeO}_2$  coating consisted of several subsidiary Y123 nucleations, while the surfaces with  $\text{CeO}_2$  coating consisted of additional Y123 grains. It causes the difference in the levitation force of the samples whose top surfaces were removed.

Fig. 7 shows the microstructure of (a) compact/coating interface, (b) high magnifications of the coating layer and (c) Y123 matrix adjacent to the interface. The coating layer is about 200 microns in thickness. In the coating layer, many square-shaped particles with a size of a few

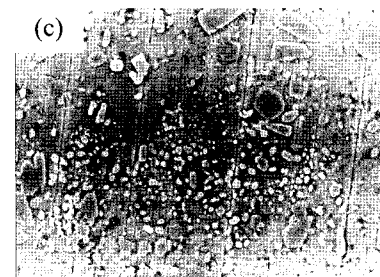
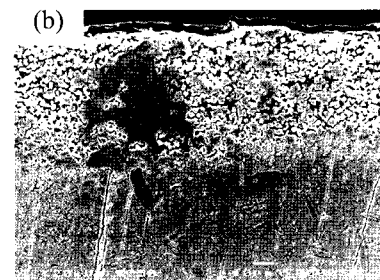
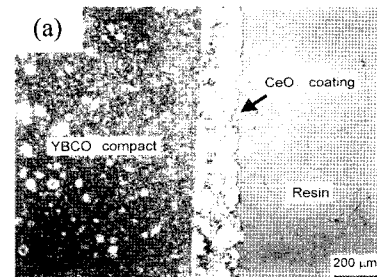


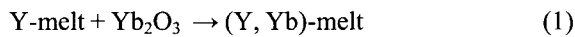
Fig. 7. Microstructure of the compact/coating interface (a) and the high magnification of the coating layer (b) and the compact region adjacent to the interface (c).

microns are observed (Fig. 7(b)). The compound formed at the compact surface was analyzed by X-ray diffraction and the data is shown in Fig. 8. The particle phase was confirmed as  $\text{BaCeO}_3$  formed by a reaction of  $\text{CeO}_2$  with the Y123 compact. In addition to  $\text{BaCeO}_3$  particles,  $\text{CuO}$  and  $\text{BaCuO}_2$  were formed as by-products of the Y123 solidification reaction. The  $\text{BaCeO}_3$  particles are concentrated in the coated region and hardly observed in the Y123 matrix, which indicates that  $\text{CeO}_2$  diffusion into the sample interior wasn't so fast.

Another characteristic feature of  $\text{CeO}_2$  coating is the formation of fine Y211 particles in the Y123 region near the  $\text{CeO}_2$  coating layer. As can be seen in Fig. 7(c), many Y211 particles are trapped within the Y123 matrix. Some of them are as large as a few microns, while others are less than a micron in size. The fine Y211 particles are attributed to the Y211 refining effect of  $\text{CeO}_2$  [13].

#### 4. DISCUSSION

This study shows the  $\text{CeO}_2$  coating effectively suppresses the surface Y123 nucleation in a top-seeded melt processed YBCO superconductor. The main concept of suppressing the Y123 nucleation at the compact surface is to produce a melt with a m. p. lower than that of the peritectic melt. The typical example is the (Yb,Y)-solid solution melt formed by the  $\text{Yb}_2\text{O}_3$  coating [9]. At the partially molten state of the YBCO compact, Yb atoms diffuse into the peritectic melt formed at the compact / coating interface and then it forms the lower m. p. melt following the equation given by,



Since the melting points of (RE,Y)123 (RE: rare-earth elements) are a function of the type of RE, the solidification temperature of a (Yb, Y)-melt lies between the m. p. of  $\text{Yb}123$  and that of Y123. During a slow cooling through  $T_p$ , a Y123 grain grows on the top surface of the Y123 compact

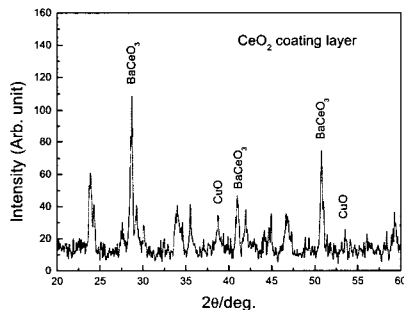
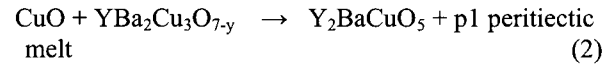


Fig. 8. X-ray diffraction pattern of the phases developed near the compact/coating interface.

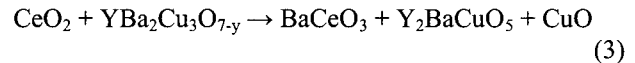
, but the (Yb, Y)-melt formed at the compact/coating interface does not solidify. The solidification of the (Yb, Y)-melt in the coated regions is thus retarded until the temperature decreases further.

The  $\text{CuO}$  coating can suppress the surface Y123 nucleation, and its role was similar to the  $\text{Yb}_2\text{O}_3$  coating [11]. The  $\text{CuO}$  reacts with Y123 powder to form Y211 and the p1 peritectic melt following the equation given by,



The m. p. ( $950^\circ\text{C}$ ) of the p1 peritectic melt is lower than the m. p. ( $1010^\circ\text{C}$ ) of the peritectic melt of Y123. A Y123 grain nucleates on the top surface and grows toward the sample interior, but no Y123 grain nucleates in the compact surface.

Compared to the above two coating materials ( $\text{Yb}_2\text{O}_3$  and  $\text{CuO}$ ), the reaction between  $\text{CeO}_2$  and the Y123 compact do not form a melt with a lower m. p. directly. The  $\text{CeO}_2$  first reacts with the barium of the Y123 compact to form  $\text{BaCeO}_3$  prior to melting following the reaction given by,



$\text{BaCeO}_3$  and  $\text{Y}_2\text{BaCuO}_5$  are stable solids, but  $\text{CuO}$  is a reactive phase. It reacts with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  forming a melt with a lower m. p according to the eq. (2). This reaction mechanism could be confirmed by the x-ray analysis ( $\text{BaCeO}_3$ ) and the microstructural evidence ( $\text{CuO}$  and Y211 near the interface) already observed in Figs. 7 and 8, respectively. The p1 peritectic melt suppresses the surface Y123 nucleation in the  $\text{CeO}_2$  coated regions like the case of the  $\text{CuO}$  surface coating [11].

#### 5. CONCLUSIONS

The effect of  $\text{CeO}_2$  coating on the surface nucleation of top-seeded melt growth processed YBCO superconductors was investigated. It was found that the surface nucleation was effectively suppressed when the surface of the YBCO compact was coated with  $\text{CeO}_2$ . The  $\text{CeO}_2$  reacts with a Y123 phase to form a  $\text{CuO}$  and Y211 phase. The  $\text{CuO}$  reacts with the Y123 phase and then produces a p1 melt whose m. p. is lower than that of the peritectic melt. Even at temperatures where a Y123 grain nucleated at the top surface, no Y123 nucleation occurred in the coated region due to the formation of the p1 melt. The fabrication of a single grain YBCO superconductor is thus easier in the coated sample than the sample without coating. The  $\text{CeO}_2$  coating gave an additional advantage of producing fine Y211 particles around the compact/coating interface.

#### ACKNOWLEDGEMENT

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