Reaction of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Superconducting Film with YSZ Substrate and Crystal Orientation in the Film

Yoshio MASUDA, Kazuo MATSUBARA*, Rikuro OGAWA, Yoshio KAWATE and Sumio SAKKA**

Superconducting & Cryogenic Technology Center, Kobe Steel, Ltd., 1-5-5, Takatsukadai, Nishi-ku, Kobe-shi 651-22

*Kobelco-Institute, Inc., 1-2-8, Wakinohama-cho, Chuo-ku, Kobe-shi 651

**Institute for Chemical Research, Kyoto University, Gokasho, Uji-shi 611

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ 超伝導膜の YSZ 基板との反応と配向

増田喜男・松原一夫*・小川陸郎・川手剛雄・作花済夫**

(株)神戸製鋼所超電導・低温技術センター, 651-22 神戸市西区高塚台 1-5-5

*(株)コベルコ科研, 651 神戸市中央区脇浜町 1-2-8

**京都大学化学研究所, 611 宇治市五ヶ庄

[Received January 11, 1993; Accepted March 16, 1993]

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (123 or YBCO phase) films were prepared on YSZ substrates by the sol-gel method. The reaction between the YBCO film and the YSZ substrate, the *c*-axis orientation of the 123 crystals in the film, and their influence on the critical current density (J_c) and the critical temperature (T_c) have been investigated. When the coating films were fired at temperatures higher than 950°C, the films reacted heavily with the substrate, the *c*-axis orientation of the 123 crystals in the films perpendicular to the substrate increased, and the 123 phase in the films changed to the 211 phase and further to the 202 phase as the reaction of the films with the substrate progressed. It has been found that J_c and T_c were improved as the *c*-axis orientation of the films increased and the film-substrate reaction decreased, indicating that the orientation of films increased as the film-substrate reaction was reduced when the volume fraction of the BaZrO_3 formed by the film-substrate reaction was between about 5 and about 13%.

Key-words: YBCO superconducting film, Sol-gel method, YSZ substrate, Reaction with substrate, Orientation, T_c , zero

1. Introduction

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (abbreviated to 123 or YBCO phase) superconducting films are usually prepared on single crystal substrates of SrTiO_3 ^{1,2)} and MgO ,^{3,4)} or on ceramic substrates of yttrium stabilized zirconia (YSZ).⁵⁻⁷⁾ It is known that the coating film reacts with the YSZ substrate, and the resultant impurity phases such as BaZrO_3 impair the superconducting properties of the films.^{6,7)} It is also known that the *c*-axis orientation of the superconducting crystals perpendicular to the substrate is effective for increasing the critical current density (J_c).^{8,9)} In our previous studies,^{5,6)} YBCO superconducting films were prepared on YSZ substrate by the sol-gel method, and properties of the films were investigated. In this article, the reaction of the YBCO film with the YSZ substrate, the *c*-axis orientation of the

123 crystals in the film, and the dependences of T_c and J_c on the film reaction and the film orientation will be described in detail.

2. Experimental procedures

2.1 Preparation of sols

Metal alkoxides $\text{Y}(\text{OC}_2\text{H}_5)_3$ and $\text{Ba}(\text{OC}_2\text{H}_5)_2$ and $\text{Cu}(\text{OCOCH}_3)_2$ were used as starting materials. These materials were dissolved in mixed organic solvents consisting of propanol, ethylene glycol and dimethylformamide to make a homogeneous solution. The ratio of metals in this solution was adjusted to the composition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. This solution was subjected to hydrolysis and condensation reactions under the acidic condition made by adding acetic acid at about 70°C. The preparation procedure of the sol is in detail described in the other papers.⁵⁾ The resultant sol was employed for coating.

2.2 Coating procedure

Films were formed by spraying the sol on the yttrium stabilized zirconia (YSZ) substrates heated at 300°C. The films were then calcined at 500°C or 800°C. The film thicknesses were adjusted to 1–20 μm by repeating the cycle of spray and calcination.

2.3 Firing and annealing

The calcined films were fired at 850 to 970°C for 2 min to 5 h, and then annealed at 450°C for 10 h. Both calcination and annealing were carried out in a pure oxygen flow of 0.5 l/min.

2.4 Identification of crystalline phases

Crystalline phases, which were formed in the fired films, were identified by X-ray diffraction (XRD) with a Rigaku Denki model RU-300 X-ray diffractometer using $\text{Cu K}\alpha$ radiation.

2.5 Scanning electron microscope (SEM) observation

The microstructure of the film was examined with a Hitachi Ltd. model S-800 scanning electron microscope (SEM). The areas having special features were analyzed by the energy dispersive X-ray spectroscopy (EDX).

2.6 Distribution of elements around the film-substrate boundary

The distribution of elements around the boundary between the film and the substrate was investigated with a Shimadzu Corp. model EMX-SM electron probe microanalyzer (EPMA). Color mapping of the elements distribution was also made. The volume fraction of BaZrO_3 and CuO layers formed near the boundary as a result of the film-substrate reaction was examined with an image analyzer.

2.7 Superconducting properties

The resistivities of the films were measured by the DC four-probe method using indium as an electrode materials. The current was kept at 1 mA. The temperatures which first generate the voltage of $0.1 \mu\text{V}$ were adopted as temperatures showing zero resistance ($T_{c,zero}$).

The critical currents were measured at 10 K in zero magnetic field, and the generated voltage of $0.1 \mu\text{V}$ was adopted as a criterion for determination of the critical currents. The critical current densities (J_c) were calculated from the critical current and the cross section area of films.

3. Results

3.1 Reaction of the film with the YSZ substrate

Typical XRD patterns of $1 \mu\text{m}$ thick coating films fired at 850, 920 and 950°C are shown in Fig. 1. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (123 phase) is already formed by firing at 850°C . In the film fired at 920°C for 30 min, no other crystals than the 123 phase are found, but the reflection peaks at 47° and 58° of the 123 phase split more clearly than those of the film fired at 850°C

Fig. 1. XRD patterns of the films obtained by firing gel films under the various firing conditions, 850°C for 30 min (A), 920°C for 30 min (B) and 950°C for 10 min (C).

○: $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, □: Y_2BaCuO_5 , △: $\text{Y}_2\text{Cu}_2\text{O}_5$, ▲: CuO , ■: BaZrO_3 , ×: YSZ substrate.

due to an increase of the 123 phase having the orthorhombic symmetry.¹⁰⁾ No secondary phases, which might result from the reaction of the film with the substrate and the decomposition of the film, are seen under these firing conditions. When the firing temperature is raised to 950°C , BaZrO_3 , Y_2BaCuO_5 (211 phase) and CuO are formed for a shorter firing duration. BaCuO_2 formed in a bulk sample, which is described in another paper¹¹⁾ of ours, is not observed.

Degree of the reaction of the film with the substrate was expressed by the 123 phase content in the $1 \mu\text{m}$ thick film. The X-ray reflection peak height ratio of the 123 phase versus the sum of peak heights of the 123 phase and BaZrO_3 , namely, 123 phase/(123 phase + BaZrO_3) was used as a measure. The peaks from $2\theta = 22^\circ$ {(003) and (100) planes}, 32° {(103), (110) and (013) planes} and 40° {(113) plane} were employed for the 123 phase, and the peaks from $2\theta = 43^\circ$ {(200) plane} and 53° {(211) plane} were employed for BaZrO_3 .

Figure 2 shows change of the 123 phase content in the $1 \mu\text{m}$ thick films fired at 850, 920 and 950°C . The 123 phase contents are decreased by the increase of BaZrO_3 formed by the reaction between the film and the YSZ substrate and the decomposition of the 123 phase. As seen from this figure, the 123 phase content remains constant at 100% during 5 h firing at 850°C . At 900°C , the 123 phase content is reduced on 2 h firing due to the reaction of a part of the 123 phase with the substrate, and remains almost constant thereafter. At 920°C , the 123 phase disappears after 2 h-firing, changing to the 211 phase. At 950°C , the 123 phase decreases to about 70% in 10 min, changing to the 211 phase, and $\text{Y}_2\text{Cu}_2\text{O}_5$ (202 phase) is present in 30 min, probably due to a loss of Ba element from the film as a result of the reaction of the film with the substrate. This loss of Ba element agrees with the reports by Manabe et al.¹²⁾ and Chen et al.⁷⁾

A typical distribution of the metal elements around the boundary between the film and the substrate is shown in Fig. 3. The film fired at 950°C for

Fig. 2. Time changes of content of the 123 phase in films on YSZ substrates fired at 850, 900, 920 and 950°C .

30 min was used for this study. Ba, Y and Cu elements are concentrated separately at the immediate boundary. It was found with an EDX analyzer that crystalline phases BaZrO_3 , the 211 phase, and CuO are precipitated. The 123 phase was not detected clearly. The morphologies of these phases are shown in Fig. 4. The particle in the BaZrO_3 layer has a similar morphology as that of the YSZ particle. The CuO layer has a smooth surface and lies on the BaZrO_3 layer. Estimation of the element distribution with an image analyzer indicated that the quantity of the CuO layer increases in proportion to that of the BaZrO_3 layer.

3.2 Orientation of the crystal in films

The c -axis orientation of the 123 phase crystals in the films was calculated using the X-ray reflection peak height ratio of $(002)/[(103) + (110) + (013) + (002)]$. The c -axis of the 123 phase crystals in the

Fig. 3. A typical distribution of the metal elements around the boundary of the film and YSZ substrate. The film was fired at 950°C.

Fig. 4. Morphology of the boundary of the film and YSZ substrate and EDX analyses of the specified parts.

Fig. 5. Dependence of c -axis orientation of the 123 grains in the films on film thickness. The films were fired 920, 950 and 970°C.

films aligned perpendicularly to the substrate surface. The degree of alignment was higher for the calcination at 800°C than for the calcination at 500°C, when the films were fired above 920°C after calcination.

The film thickness dependence of c -axis orientation of the crystals in the films, which were fired at 920, 950 and 970°C, is shown in Fig. 5. The c -axis orientation increases as the film thickness decreases and as the firing temperature is raised. However, in the films with a thickness less than about 3 μm , most of the 123 phase once formed disappears due to an intensive reaction of the film with the substrate when the films are fired at temperatures higher than 950°C. When the film thickness is larger than 10 μm , some of the 123 phase is still remaining, the orientation decreases to less than 20%, and the film surface becomes coarse. These indicate that the maximum c -axis orientation of the 123 phase crystals in the films is about 40% under the condition where the 123 phase is little impaired by the film-substrate reaction.

The SEM images of the surfaces of the films fired at 920, 950 and 970°C are shown in Fig. 6. It is seen that grains of the 123 phase grow as the firing temperature increases, accompanying an increase of the c -axis orientation. Especially, when the film is fired at 970°C, the 123 phase grains grow much, and small particles are deposited in large grains of the 123 phase. These particles are considered to be the 211 phase from the result of XRD study.

3.3 Dependence of the superconducting properties on the reaction of the film with the YSZ substrate

Figure 7 shows dependences of the superconducting properties, J_c and $T_{c,zero}$, on the reaction of the film with the YSZ substrate. The degree of the film reaction is expressed by the volume fraction of BaZrO_3 phase, $\text{BaZrO}_3/(\text{BaZrO}_3 + \text{film}) (\%)$.

BaZrO_3 is a phase formed by the film-substrate

Fig. 6. SEM images of the film surfaces fired at 920°C (a), 950°C (b), and 970°C (c).

Fig. 7. Dependences of J_c and $T_{c,zero}$ on film reaction which is expressed by the ratio of volume of the produced $BaZrO_3$ to that of films.

reaction.

It is found that the dependences are divided into two regions. Each region is dependent on the firing temperature. In firing at temperatures lower than 900°C, the volume fraction of $BaZrO_3$ is less than about 3 %, while in firing at temperatures higher than 920°C, the fraction is larger than 4 %. The maximum values of J_c and $T_{c,zero}$, $J_{c,max}=240$ A/cm² and

Fig. 8. Dependences of J_c and $T_{c,zero}$ on film orientation.

$T_{c,max}=87$ K, are obtained at the condition where the volume fraction of $BaZrO_3$ is about 5 %. J_c and T_c markedly decrease as the volume fraction increases above 5 %, further the superconducting current almost disappears when the volume fraction of $BaZrO_3$ reaches about 13%.

3.4 Dependence of the superconducting properties on the film orientation

Figure 8 shows dependences of the superconducting properties, J_c and $T_{c,zero}$, on the c -axis orientation of films. It is seen that the superconducting current is not obtained when the orientation is less than about 5 %. The volumes of J_c and $T_{c,zero}$ increase as the orientation increases up to about 35%. These values decrease when the orientation is higher than about 40%.

4. Discussion

4.1 Reaction between the coating film and the YSZ substrate

The reaction between the coating film and the YSZ substrate is the most serious problem encountered in the preparation of the YBCO superconducting film on the substrate. As shown in Figs. 1 and 2, BaO in the film reacts with ZrO_2 in the substrate at high temperatures, leading to the decomposition of the superconducting phase into non-superconducting phases containing a smaller amount of Ba than the YBCO phase does. The reaction may be expressed as follows.

Around 900°C, the 123 phase formed in the film starts to react with the YSZ substrate, forming BaZrO_3 , according to Eq. (1). This reaction is carried out in the solid state and is consistent with the results reported by Manabe et al.¹²⁾ At higher temperatures around 950°C, the 123 phase melts incongruently,¹³⁾ forming the 211 phase and a Ba-Cu-O liquid phase, according to Eq. (2). Equations (3) and (4) indicate that the Ba-Cu-O liquid phase easily reacts with the substrate, forming BaZrO_3 . These facts suggest that when the coating films are fired at around 950°C, firing should be done for a short duration, e.g., several minutes, in order to reduce the reaction of the film with the substrate.

The result that the quantity of BaZrO_3 is in proportion to that of CuO suggests that the assumed four equations, in which BaZrO_3 and CuO are concurrently formed, are reasonable.

4.2 Relationship between the orientation and the reaction of the film

Comparison of Fig. 8 with Fig. 7 indicates that the c -axis orientation of films decreases from 35% to 5% as the volume fraction of the BaZrO_3 phase, which is a phase formed by the film-substrate reaction, increases from 5% to 13%. The orientation in this range, which is derived from comparatively thick films above 8 μm in thickness, is found in the presence of the Ba-Cu-O liquid phase. It is assumed that the Ba-Cu-O liquid phase separates more clearly from a layer of the 123 phase as the film thickness increases, and the reaction of the film with the YSZ substrate is carried out effectively with the separated liquid phase, increasing BaZrO_3 . On the other hand, the c -axis orientation of the 123 phase grains is assumed to be difficult for the films with the thickness of above 8 μm , because of the absence of the liquid phase.

The relationship between the c -axis orientation of the film and the film-substrate reaction is shown in Fig. 9. There are three regions, A, B and C. Region B corresponds to the results shown in Figs. 7 and 8

Fig. 9. Relationship between film reaction and film orientation.

which are discussed above. In regions of A and C, the orientation of the film increases as the reaction of the film with the substrate is promoted. That is to say, when the films are fired below 920°C, the reaction of the film is not so heavy, and the film orientation does not effectively occur, because the Ba-Cu-O liquid phase may be absent. This state corresponds to Region A. When the thickness of films is below about 3 μm and the films are fired at above 920°C, the film orientation increases as the film reaction increases, and the 123 phase disappears when the film reaction is too severe. This state corresponds to Region C. This fact may be explained by the assumption that a large amount of the Ba-Cu-O liquid phase is formed at high temperatures, and the liquid phase does not separate from the layer of the 123 phase in the films, because of the thinness of the films. This causes the film reaction and the film orientation to make progress concurrently.

Region B was favorable for increasing the film orientation and reducing the film reaction, but the film orientation did not increase above 40%.

5. Conclusions

The reaction of the YBCO superconducting film with the YSZ substrate, the c -axis orientation of the film, and the influence of these on J_c and T_c properties were studied. The following results were obtained.

(1) When the coating films were fired at temperatures higher than 950°C, the reaction of the film with the substrate and the orientation of the 123 crystals in the film progressed intensively, probably due to formation of a Ba-Cu-O liquid phase. The 123 phase in the film formed on the substrate changed to the 211 phase and further to the 202 phase as the film-substrate reaction progressed.

(2) CuO, BaZrO_3 and the 211 phase were formed separately near the boundary between the film and the substrate as a result of the reaction of the film with the substrate.

(3) J_c and T_c properties were improved as the orientation of the film increased and the reaction of the film decreased. It was found that the orientation of the film increased as the film-substrate reaction decreased when the volume fraction of BaZrO_3 reaction phase was between about 5 and 13%, but the orientation of the film did not increase above 40%.

(4) A thick film, of which $T_{c,zero}$ was 87 K and J_c was 240 A/cm², was obtained by controlling the film reaction and the film orientation.

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