2005년도 추계 학술발표대회 발표논문, 2005년 11월, 경남 산청

플라즈마 용사 및 열처리 공정을 통한 Bi-2212/2223 초전도체 thick film 제조의 기술 개발

Technique development of Bi-2212/2223 superconductor thick film manufacturing by plasma spraying and heat treatment

Seon-Hong Lee*, Sang-Hum Cho, Young-Bong Ko, Kyeung-Chae Park
* Department of Metallurgic Engineering, Kyungpook National University

ABSTRACT $Bi_2Sr_2CaCu_2O_x$(Bi-2212) and $Bi_2Sr_2Ca_2Cu_3O_y$(Bi-2223) high-T_c superconductor(HTS) coating have been prepared by plasma spraying and heaat treatment. The Bi-2212 HTS coating layer is synthesized through the peritectic reaction between Sr-Ca-Cu oxide coating layer and Bi-Cu oxide coating layer, and $Bi_2Sr_2CaCu_2O_y$ (Bi-2212) superconducting phase grow by partial melting process. The superconducting characteristic depends strongly on the conditions of the partial melting process. The Bi-2212 HTS layer consists of the whiskers grown in the diffusion direction. Above the 2212 layer, Bi-2223 phase and secondary phase was observed. The secondary phase is distributed uniformly over the whole surface. This is caused to the microcrack on the coatings surface. Despite everything, the film shows superconducting with an onset T_c of about 115K. There are two changes steps. One changes (1step) at 115K is due to the diamagnetism of the Bi-2223 phase and the other changes (2step) at 78K is due to the diamagnetism of the Bi-2212 phase.

1. Introduction

$Bi_2Sr_2CaCu_2O_x$ (Bi-2212)is one of the most promising high critical temperature (T_c) superconductors for industrial applications because of its high T_c and easy formation of microstructure. Also $Bi_2Sr_2Ca_2Cu_2O_3$ (Bi-2223) phase is the most promising material for tapes and wire for large scale and high-current applications. However, it is very impossible to process a thick film form because the oxide superconductor is so brittle. Besides, the existing manufacture methods is very decreased of the superconductor characteristic due to shrinking transformation and damage of oxide compound.

Plasma spraying technique process, the feed stock particles are introduced into a plasma gun, where they are heated, melted and propelled out of the torch to impact on the substrate, resulting in solidification and coating buildup. This technique is used for depositing a wide variety of material and is well known for producing hard wearing and durable coatings on engineering parts.

The Bi-Sr-Ca-Cu-O system is home to a large number of phases. Their nature and stability have been excessively studied [1-2]. The formation and distribution of the phases in the micrstructure of the final Bi-2212 and 2223 component can be controlled by partial melting process parameters. This process consisting of three important steps lead to the highest critical current densities and critical temperature: heating to a maximum temperature close above the solidus to partially melt the Bi-2212, slow cooling the high temperature micro structure consist of liquid and solid secondary phases to a temperature below the solidus to enable the crystallization of Bi-2212 and annealing below the solidus to further improve the homogeneity of the micro structure [3-4].

In the present paper, on the based of optimal conditions for high critical current and temperature, we study on the possible source of Bi-2212 /2223superconductor thick film manufacture showing excellent superconductivity properties.

2. Experimental

The powder was prepared by the calcinations and ball mill process. Appropriate amounts of Bi_2O_3, CuO and $SrCO_3$, $CaCO_3$, CuO were mixed in the ratio of Bi : Cu = 2.2 :1 and Sr : Ca : Cu = 2 : 1 : 2 respectively by ball-mill process and calcined at 780°C in air for 24h. And then this calcined bulk was ball-mill one more time. After ball-mill process, it was sieved. The substrate was used to stainless steel plate (10 x 10 x 2). The material of using salt thermal spraying is general salt.

The salting thermal spray was used to flame spraying (METCO TYPE 5P). Salt powder is very impossible to feed on thermal spraying because of its high moisture absorption. To solve this problem, we created the feedstock device. After coating process was done, coating plate was into warm water for dissolved the salt coating layer. Atmospheric plasma spraying (Plasma

Dyne) was used to deposit 2001 and 0212 coatings. The spraying conditions of are shown in Table 1. Argon was used to primary plasma gas. The hydrogen gas, which involved directly with oxidation and deoxidization of oxygen, was not used to prevent the phase decomposition.

The microstructure of Bi-2212/2223 coating was examined by scanning electron microscopy (SEM), energy disperseve x-ray spectrometer (EDS) and the structure of the coating was characterized by X-ray diffraction (XRD) analysis. The sample was heated from room temperature up to 710°C at a rate of 20°C/min. From this temperature up to the highest temperature of 895°C, the rate of 1.5°C/min was applied. During heating the sample was held for 60min at the temperature of 895°C. From 895°C the sample was cooled to 850°C at the rate of 0.5°C/min. At 850°C the sample was held again during 120min. From the 850°C to room temperature the sample was furnace cooled.

Among many methods, the so-called zero- field-cooling (ZFC) and filed-cooling (FC) processes have been widely used. In a ZFC processes, the sample is cooled down from above T_c to a desired temperature in zero field. And then an external field is applied and the data are collected in the warming up process. In a FC process, the sample is cooled down from above T_c to a desired temperature with an external field, and then the data are collected in both the cooling down (FCC) and the warming up (FCW) process. The ZFC and FC magnetic moments have been measured to determine the superconducting transition temperature T_c [5].

3. Results and discussion

The mean particle size is 55μm and 68μm respectively. The longer the milling time, the more bonding between particle and particle was observed. However, the milling time was limited due to the possibility of impurity contamination from the container wall and the balls. This impurity contaminat ion was caused to decrease of the superconducting property.

Fig. 1 shows the cross-sectional SEM image of the spray coating layer; before PMP (a), after PMP (b) and a close view of 2212 whisker (c). The thickness of 2212 and mixing layer, 2223 phase and secondary phase, is about 100μm respectively. The thickness control of reaction layer was highly affected by partial melting conditions such as the maximum high temperature, cooling rate, annealing time and temperature. As shown in Fig. 1(c), the Bi-2212 layer, called whisker, was grown by the diffusion reaction between 2001 and 0212 coating layer. The width (in the direction of c-axis) of whisker, needle-like crystals, had about 50μm and the thickness (in the direction a-axis) was about 5μm. In the BSCCO system, a thick and homogeneous HTS layer of Bi-2212 is easily synthesized by the diffusion reaction between Bi-free Sr-Ca-Cu oxide substrate and Bi-Cu oxide coating [6-7]. This Bi-2212 phase is a consequence of its reformation from solid (0212) and liquid (2001) peritectic phases [8]. Fig. 1(e) presents the XRD pattern of the Bi-2212 layer after removed the 2223 and secondary phase layer. The pattern indicates strong (200) peak. This is compared with that of XRD patterns of conventionally sintered Bi-2212 bulk surface [9]. On based Fig. 1(c) and (e), the Bi-2212 layer is found to be composed of c-axis oriented grain. So, the transport current passes through the specimen along the ab planes of the grains. In Fig. 1(d) a whisker showing stripe-like morphology is presented.

Fig. 2 shows the SEM images of the coatings surface; before PMP (a), after (b), a closed view (c), (d) and XRD pattern of the coating surface (e). As shown in Fig. 2(b), the secondary phase is distributed uniformly over the whole surface. Fig. 2(c), (d) shows more detailed views of the coating surface. The terrace-like structure is very obvious in the figure. According to the analyses by XRD and EDS, the coating surface mainly consist of Bi-2223 and secondary phase (including CuO, Bi_4SrO_7, $(Sr,Ca)CuO_2$). There are several proposals regarding the formation mechanisms of the Bi-2223 phase, but the exact mechanism is not yet known. Among that, a reaction between 2212 and the liquid phase is proposed [10-11]. The liquid enhances dissolution of the 2212 phase as well as other unwanted phases [12]. So, we think that the liquid phase is important for the formation of the 2223 textured structure during cooling from the maximum temperature to annealing temperature.

The oxide superconductor is very brittle. So, a little microcrack caused to damage of the coating and negative influences to about superconducting property. As shown in Fig. 3, the microcrack formed along the secondary phase. But, we expect that these secondary phases in coatings were removed by controlled PMP.

As shown in Fig. 4, in both the ZFC and FC processes, the M(T)curve keeps flat at temperatures up to about 115K, then the curve rises up rapidly and turns flat again at T_c. As shown below the flatness of the ZFC M(T) and the FC M(T) have very different physical origin. One changes (1step) at 115K is due to the diamagnetism of the Bi-2223 phase and the other (2 step) changes at 78K is due to the diamagnetism of the Bi-2212 phase [13].

4. Conclusion

We have investigated the possibility of the thick film superconductor by plasma spraying and partial melting process. It has been found that the Bi-2212 layer, about 100μm in thickness, was formed by the peritetic diffusion reaction between 2001 and 0212 coating layer. These whiskers were consisted of needle-like and c-axis textured grains. Also, we observed the Bi-2223 phase, terrace-like and b-axis grains, and secondary phase above Bi-2212 layer. The secondary phase was caused to the microcracks on coatings surface and may be it was negative affected to the coatings life and superconducting property. Despite everything, the film shows superconducting with an onset T_c of about 115K.

References

[1] W. Paul, M. Chen, M. Lakner, Physica C, Part 3 372 (2002) 1657.

[2] T. Schweizer, R. Muller, L.J. Gauckler, Physica C 225 (1-2) (1994) 143.

[3] D. Buhl, T. Lang, M. Cantoni, D. Risold, B. Hallstedt and L.J. Gauckler, Physica C 257, 151 (1996)

[4] J. Shimoyama, N. Tomota, T. Morimoto, H. Kitaguchi, H. Kumakura, K. Togano, H. Maeda, K. Nomura and M. Seido, Jpn. J. Appl. Phys. 31, L1328 (1992).

[5] U. Welp, W.K. Kwok, G..W. Crabtree, K.G. van der Voort, J.Z. Liu, Phys. Rev. Lett. 62 (1998) 1908.

[6] K. Tachikawa, Y. Yamada, M. Satoh, Y. Hishinuma, Proceedings 1994 Topical International Cryogenic Materials Conference, World Scientific, 1995, p. 307.

[7] H. Kumakura, K. Togano, J.Kase, T. morimoto, and H. Maeda, Cryogenics 30 (1990) 919.

[8] T. Hanato, Y. Takano, A. Fukuyo, S. Arisawa, AIshii, K. Togano, IEEE Trans. Appl. Supercond. 11 (2001) 2846.

[9] M. Onoda, A. Yamamoto, E. Takayama-Muromachi, S. Takekawa, Jpn. J. Appl. Phys. 27 (1988) 833.

[10] I. Matsubara, R. Funahashi, T. Ogura, H. Yamashita, Y. Uzawa, K. Tanizoe, T. Kawai. Physica. C 218 (1993) 181.

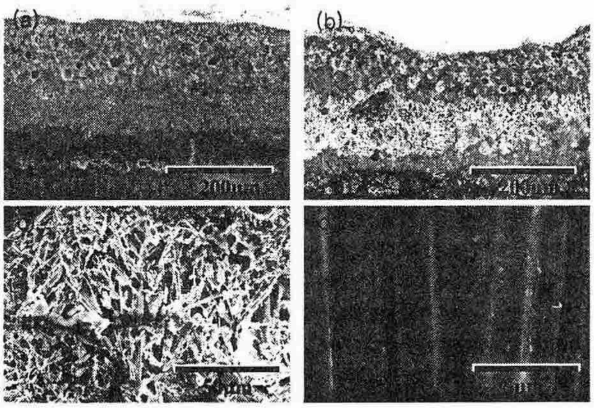
[11] Y. Ikeda, H. Ito, S. Shimomura, Z. Hiroi, M. Takano, Y. Bando, J. Takada, K. Oda, H. Kitagushi, Y. Miura, Y. Takeda, Physica C 190 (1991) 18.

[12] T. Hatano, K. Aota, S. Ikeda, K. Kakamura, K. Ogawa, Jpn. J. Appl. Phy. 27 (1998) L2055.

[13] X.Y. Lu, A. Nagata, K.Watanabe, T. Nojima, K. Sugawara, S. Hanada, S. Kamada, Physica C 392-396 (2003) 453-457.

Table 1 Bi-2212 plasma spraying conditions

Ar gas pressure (l/min)	38
H_2 gas pressure (l/min)	0
Spray distance (mm)	90
Spraying atmosphere	air
Arc current (A)	500
Voltage (V)	50
Powder feed rate (g/min)	30
Carrier gas flow (l/min)	8



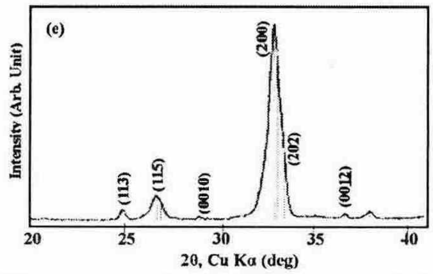


Fig .1 The cross-sectional SEM image of the spray coating layer; before PMP (a), after PMP (b), a closed view of 2212 whisker (c), parallel stripesboundary of whisker (d) and XRD pattern of 2212 layer (e)

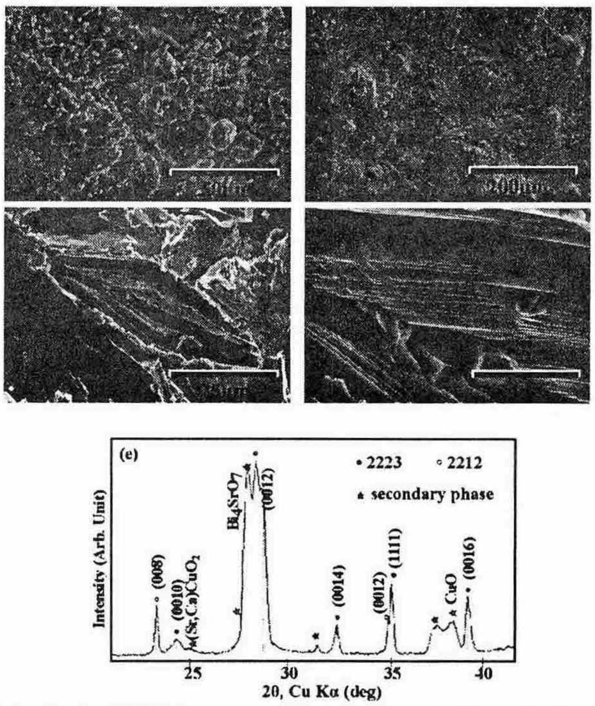


Fig. 2 the SEM images of the coatings surface; before PMP (a), after (b), a closed view (c), (d) and XRD pattern of the coating surface (e).

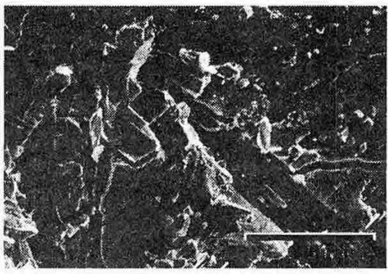


Fig. 3 The SEM image of microcrack along secondary phase

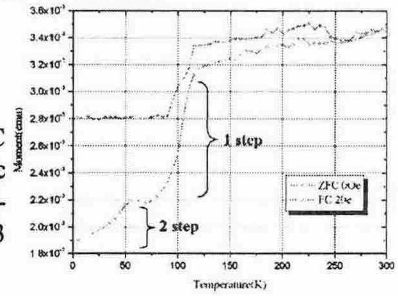


Fig. 4 The ZFC and FC magnetic moment of Bi-2212/2223 coatings.