Effect of silver oxide additions on YBCO thick film properties

Soh Deawha*, Li Yingmei*, Cho Yongjoon*, Korobova N.**

Abstract

The effect of silver oxide (14 wt.%) addition to YBCO compounds and electrophoretic deposition of composite particles prepared by solid phase reaction have been investigated. The results were compared with those for as-processed samples with YBCO films on Ag wire substrate. Our experiments show that the adhesion, microstructure changes, superconducting properties of these films is sensitive to the silver content and sintering conditions. Adding a small amount of PEG tends to remove cracks in the YBCO and (YBCO + Ag) films, which develop during the heating process. An attempt has been made to explain the experimental observations regarding variation of critical current density with the YBCO and (YBCO + Ag) films.

Key Words : silver addition, solid phase reaction, cracks, critical current density

1. INTRODUCTION

Since the discovery of high-T_c oxide superconductors, many efforts have been made to develop the practical application of these new materials. A number of fabrication approaches have been studied due to the inherent brittleness of ceramic materials and the difficulties in forming the high T_c superconductor into desired shapes. Thick film fabrication technique have been videly investigated because of the prospect of coating superconducting materials on a variety of substrates and surfaces offers a number of promising advantages for large scale as well as electronic device applications [1,2].

It is well known that silver addition into the bulk of YBCO [3] facilitates oxygen diffusion and helps in improving the stability of superconductors towards moisture. It was found that maximum value of Ag contents must be 14 wt.%, (textured bulk YBCO + Ag ceramics prepared by MTG had $J_c \approx 7 \times 10^4$ A/㎠) [4].

In this work the results of investigations on the effect of silver addition for new composite materials including Y_2O_3, BaO, CuO and Ag_2O powders as starting materials on the superconducting properties of YBCO thick films electrophoresed on silver substrate are presented in correlation with the phase and microstructural changes. Our results show that the superconducting properties and microstructure of these films are sensitive to the sintering conditions.

2. SAMPLE PREPARATION AND EXPERIMENT

The powder of (YBCO + Ag) was prepared by calcining the mixture of appropriate amounts of commercial YBCO and Ag_2O powders as starting materials at 970 ℃ in the air for 0.5 h with one intermediate grinding to ensure better homogeneity. The silver content in this composite compound was 14 wt.% by weight. According to the X-ray analysis, all film samples annealed at 890 and 900 ℃ are strictly single-phase and correspond to a

* : Myongji University, Korea,
(E-mail : dwhsoh@wh.mju.ac.kr)
** : Combustion Problems Institute, Kazakstan
(E-mail : icp@nursat.kz)

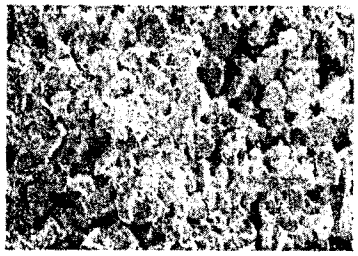
well-crystallized compound with orthorhombic symmetry. The measured oxygen content does not differ from the standard value of x = 6.8 ~ 6.9 inherent in fine-grained samples. Sintered compound consists of friable agglomerates of fine particles 1.0 ~ 5.0 ㎛ in size. Dispersing 0.25 g of (YBCO + Ag) powder (-400 mesh) in 25 ㎖ distilled acetone made the powder suspension. The deposition always occured at the cathode. At present the electrochemical aspects of the deposition process are being studied, as the mechanism of charging is not fully understood. Coatings were deposited by electrophoresis method on Ag wire at 100 ~ 400 V/cm and 15 ~ 120 s. The density of the unfired, as-deposited coating (50 % of theoretical) was found to be virtually independent of the applied voltage. After the coatings were dried at 100 ℃, they were heated slowly (at a rate of 2 ℃/min) up to 890 ~ 900 ℃ in the air. The thickness of a deposited coating was usually in the range of 10 ~ 60 ㎛. Precise thickness depended upon deposition conditions (voltage and time) and nature of suspension (particle size and concentration). The heat-treated films were about 80 % dense and were characterized with X-ray diffraction, optical microscope. Microstructures of these films were examined by scanning electron microscopy (SEM) (JSM-T200, JEOL, Tokyo, Japan). The critical current density was measured by dc standard four-probe method. The measurements were performed at 77 K using indium solder contacts. The critical current was defined, as the current required generating an electric field of 10 V/cm between the potential probes.

3. EXPERIMENTAL DATA AND ANALYSIS

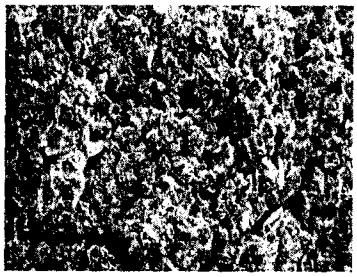
Electrophoretic deposition is based on the principle that ceramic powder suspended in a liquid vehicle attains a surface charge. The charged particles will move under the influence of an electric field and deposit on an electrode. The reason for the low values of T_c and J_c can be attributed to the random orientation of the crystallites, poor grain interconnectivity, and film degradation due to the interaction between the film and substrate.

In this work in addition to the superconducting particles suspension we used a nonionic polymeric binder, such as poly(ethylene glycol) (PEG). The primary purpose of this polymer phase is to increase strength and toughness of the green body. Polymer chains can adsorb simultaneously on the surface of particles, leading to "bringing" between them. Although this bridging effect is desired in the dried green state, it also may occur to some extent in the suspension, thereby promoting undesirable bridging flocculation. The effect of added polymers is highly dependent on the adsorption behavior of the polymer chains on the particles.

By this method, thick HTS films up to 60 ㎛ thickness have been made. SEM images typical of the optimized YBCO and (YBCO + Ag) films are shown in Fig. 1. (a, b). The particle-size distribution is narrow (3 ~ 5 ㎛), with a majority of the particles being 3 ㎛.



(a)

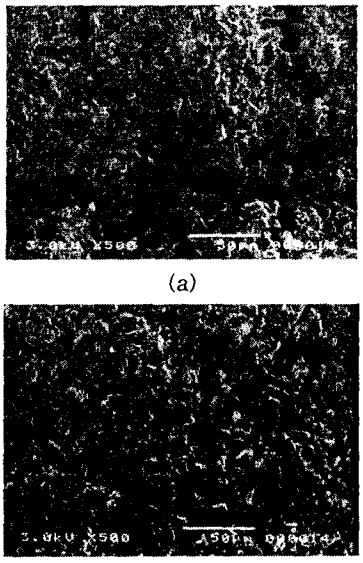


(b)

Fig.1. Scanning electron micrographs of YBCO (a) and (YBCO + 14 wt.% Ag) films (b).

Homogeneously distributed PEG organics was burned off below 600 ℃ prior to texturing under

controlled conditions and the remaining pores were very small and can easily be densified at lower temperature. However, the extent of porosity varies with compositions and sintering schedules. It is seen that, on increasing amount of PEG addition, and fine structure appear to grow, the effect of which on physical properties, if any, is not very clear and warrants further studies. Scanning electron microscopy photograph of the fractured surface of (YBCO + Ag) films shows the compacts with larger grains of a few micrometers size and smaller submicron grains dispersed Fig.2. (a, b). You can see that the grains bonded tightly and the fracture occurred by both transgranular and intergranular modes.

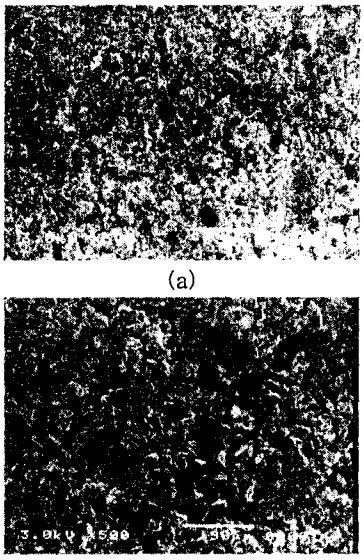


(a)

(b)

Fig.2. SEM micrographs of (YBCO + Ag) films electrophoresed in acetone suspension with the same conditions: (a) without polymer, (b) with addition of 2 ㎖ 1 % PEG-1000.

The results show the best films with addition of PEG. Dehydration and removal of the organic residue increased with increasing the concentration of polymer to a critical concentration, above, which these decreased. The weight loss is not proportional to the concentration of polymer as a dispersant. SEM micrographs for YBCO and (YBCO + Ag) films as an example of silver addition and polymer binder influence on the microstructure of electrophoretic deposited films are shown on Fig.3.



(a)

(b)

Fig.3. Micrographs for YBCO film (a) and (YBCO + Ag) film (b) with PEG addition

For the interaction between polymers and oxides, explained in detail in [4], the viscosity of the suspension with polymer was higher than that of the suspension without polymer. The reason for this is the high molecular weight of the polymer itself (we used PEG with 1000).

4. DISCUSSION

It is evident that the sintering conditions (MTG or solid state reaction) and polycrystalline structure in the bulk or film samples play a significant role in the determination of the microstructure of sintered barium yttrium cuprate (123) samples. However, over the range of conditions examined here, there does not appear to be any correlation between microstructural features, such as average grain size and the transport J_c.

It was found that the J_c value of the samples is also had strong microstructure and thickness

dependence. For example, for YBCO films with thickness from 30 to 55 ㎛ $J_c \approx$ (450 ~ 300 A/㎠) and for (YBCO + Ag) films with thickness from 15 to 30 ㎛ $J_c \approx$ (450 ~ 400 A/㎠) with the same conditions of preparation. Molecular packing and film density play a crucial role in determine the characteristic of the green and sintered film specimens. The high packing density satisfies the conditions for a pore-free and dense, sintered electrophoretic film. Addition of a polymer enhances the strength, flexibility, and workability of YBCO in its green state, before sintering. So in our case we can conclude, that it might be preferable for the polymer to function not only as a dispersant but also as a binder. The films sintered at the same conditions, thickness (30 ㎛) and same additions of PEG (2 ㎖) provided $J_c \approx$ (1200 ~ 1300 A/㎠ for YBCO films and $J_c \approx$ (500 ~ 600 A/㎠) for (YBCO + Ag) films.

It suggests that the J_c value smaller than two times for silver addition may be correlated to an increased amount of additional phases. The J_c value between 400 (without polymer) and 500-600 A/㎠ (with PEG addition) is believed to be governed mostly by the weak link mechanism and poor grain-to grain connectivity leading to deterioration of junction characteristics, which in turn reduces the junction J_c. This observation is somewhat unexpected in view of the well-known diffusion and incorporation of oxygen into the bulk of the sample due to the presence of silver.

We conclude, that silver has been introduced by different methods (MTG and solid reaction) can result in different morphologies and physical properties. Therefore, the overall J_c of the sample gets modulated depending on the morphology [5] and resultant non-uniformity in the distribution of the transport current.

5. CONCLUSION

Electrophoretic deposition offers a novel approach for superconducting coatings on a variety of shapes including wires and coils as well as plates. The quality of the samples prepared by the EPD technique has been closely studied. For thinner coatings, the grains are smaller yet uniform in size with good connectivity, while in the higher thickness regime exaggerated grain growth takes place, which leads to a certain amount of porosity and microcracks. Since the coating must be sintered to temperatures above 900 ℃ to achieve necessary density and superconductivity, it is essential to control the interfacial reactios which occur at the coating/substrate interface. Silver substrates were found to be inert with YBCO and gave no evidence of the intermediate layer. Our results show that superconducting properties and microstructure of these films are sensitive to the silver content for bulk and film samples and sintering conditions. J_c is lower in (YBCO + Ag) films as compared to the bulk samples, which may be due to the larger amount of the 211 phase present in the films. Under the present processing conditions, our results indicate that metallic silver powder is more useful than silver oxide in enchancing the superconducting properties.

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