# High Temperature Superconducting (HTS) Films by EPD Method addition with $BaF_2$ and PEG

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ABSTRACT

High temperature superconducting films deposited on metal Ag wire were prepared with YBCO powders by electrophoretic deposition method. $I_2$ was used as additives for surface charge of YBCO particles. When 2~3 wt.% $BaF_2$ was added in the YBCO suspension, the pores and cracks of film surface were decreased and film density could be increased. In case of YBCO films, the critical current density ($J_c$) was calculated at the value of 1458 A/cm$^2$ (77K, 0K) by 4 point prove method.

**Key words**: electrophoretic deposition, YBCO, BSCCO, critical current density, superconducting wire

## 1. Introduction

The preparation of superconducting wire is the important techniques for a wide range of application of these materials. To date, various approaches, such as OPIT, IBAD, RABiTS, Spraying and Dip coating techniques have been investigated to prepare superconducting wires and tapes.[1] Electrophoretic deposition (EPD) is a promising technique for small and large-scale devices as well as electronic and electrical devices. In this technique, fine particles, typically a few microns, are suspended in an organic dielectric solvent. The application of a dc voltage of 50-400 Volts between two electrodes causes the particles to move and deposit. EPD is a combination of two processes: electrophoresis and deposition. Electrophoresis is the motion of charge particles in a suspension under the influence of an electric field. Deposition is the coagulation of particles to a dense mass. The present paper researched both electrophoresis and deposition. The kinetics and applications of EPD to HTS films also was examined. The advantages of this method are: (1) obtaining an uniform and dense coating, (2) controlling easily the coating thickness by the deposition voltage and deposition time, (3) obtaining various shapes and sizes of coating on various substrates, (4) the thickness of the silver need only be sufficient to allow the round fiber to be rolled. In the PIT case, it must be thick and strong enough to allow the drawing process to be performed. Thus, the superconductor to silver ratio can be much higher for the electrophoretically formed tapes compared to those made using PIT processing, (5) to fabricate as-deposited superconducting thick films with highly *c*-axis oriented grains (the particle orientation is controlled right during the particle deposition).[2~5] In this report, the thick films of YBCO was prepared by electrophoretic deposition method using powder dispersed in acetone or alcohol. The conditions and processes of electrophoretic deposition for (HTS) thick films were studied in detail.[6]

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Morphologies of the calcined and sintered films were examined with a scanning electron microscope (SEM) Hitachi Manufacturing Company model S-800. Phases generated in the film and products as a result of the reaction of the film and substrate were identified by X-ray diffraction (XRD) with a Rigaku Denki model RU-300 X-ray diffractometer using $CuK_\alpha$ radiation. Resistivities of the films were measured by a DC 4-probe method using a silver metal electrode with a current of 1 ㎃. The zero resistivity temperatures were determined by the criterion of 0.1 ㎶.

## 2. Experimental results and discussion

### 2.1 Electrophoretic deposition

YBCO superconducting thick films were deposited by electrophoresis in suspension solution with superconducting powders of which were prepared by solid state reaction and commercial use. Average particle size distribution of these powders was in range of 1 to 5 ㎛. Silver wire (0.8$\phi$) and alumina plate coated with Ag were used as substrates ("-" electrode) and stainless steel meshwork as counter ("+") electrode in the suspension solution. The distance between two electrodes was 10 ㎜. To decide the best conditions and processes for YBCO thick films in acetone suspension, the amount of deposit of YBCO powder were measured by use of electronic balance at different applied voltages, content of iodine, content of YBCO powder and temperatures. In this work we propose that electrostatic stabilization of HTS particles in butanol and acetone involves three steps:

I. Adsorption of solvent molecules in undissociated form onto the basic surface sites of the HTS particles;

II. Dissociation of the adsorbed solvent molecules by hydrogen ions transferring to the basic surface sites;

III. Desorption of $C_4H_9O^-$ anions or $C_2H_5CO^-$ into the solution, leaving the particles positively charged. The iodine $I_2$ (as a cationic surfactants) is sparingly soluble in apolar solvents and, therefore, tends to adsorb at the particle/solvent interfaces, thus charging the particles more positively.

In our previous works[7] we reported that, in organic (nonaqueous) suspensions, only mechanism of electrostatic stabilization and the mechanism of electrosteric stabilization are significant. Stable suspensions provide a dense, homogeneous deposit on the electrode.

The rate at which a deposit forms during EPD is very important if the thickness of the deposited layer is to be controlled. It has been found that the current was reduced quickly with increasing deposition time at different applied voltages, and the deposition current was enhanced with increasing applied voltages. It has been shown that the amount of deposition of YBCO powder was enhanced with increasing applied electrical potential. When the applied voltage was lower than 500 V, the amount of deposits of YBCO was increased almost linearly with increasing applied voltage. When iodine content was less than 200 mg/l in suspension, the amount of deposits was increased with increasing iodine content, but iodine content was more than 200 mg/l in suspension, the amount of deposits was reduced with increasing iodine content. So the optimum value of $I_2$ content could be determined with less than 200 mg/l for good preparation of YBCO thick film by EPD.

In order to reduce the micro-cracks developed in YBCO layer, the 0-3wt.% of $BaF_2$ were added in YBCO/acetone suspension deposited at same time on the cathode.[8] The thickness of YBCO films was 30-80 ㎛.

### 2.2 Oxygen absorption process for YBCO thick film

Because the micro-cracks on YBCO and the weak links between grain boundaries have important influence on superconductivity of YBCO superconductor, the YBCO thick film samples were not superconductive using usual heat treatment process. However, due to a large difference of the thermal expansion rate of Ag layer ($21.1\times10^{-6}$/℃ in 27-527℃) and YBCO thick film ($14.4\times10^{-6}$/℃ in 30-500℃), micro-cracks could be developed on the YBCO thick film after heat treatment resulting in a lower critical current density. Because the melting point of Ag was 96

1℃, so the temperature of heat treatment should be lower than 940℃. It could be obtained by suitable heat treatment conditions, which was shown as follow; heat the samples from room temperature to 790℃ for 5-8 hours, then heat it up to 910℃ at the rate of 0.5-2.0℃/min, stabilize them in the temperature for 12-24 hours, reduce the temperature to 650℃ for 5 hours, stabilize them again at 650℃ for 5 hours, reduce temperature to 450℃ for 4 hour, stabilize it for 48 hours in oxygen flow, and then reduce it to room temperature for 2 hours. After this long procedure the YBCO thick film samples were with Meissner effect.

### 2.3 XRD analysis for YBCO thick film.

The X-ray diffraction patterns of YBCO thick film and sintered YBCO pellet were measured by PW1710 BASED X-ray Diffractometer ($CuK_\alpha$), the results were shown in Fig.1 (a) and (b). It could be seen that the sintered YBCO pellet sample exhibited a preferred orientation with the c axis perpendicular to the sample surface.

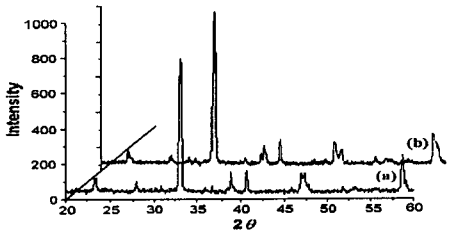



Fig.1. X-ray diffraction pattern of sintered YBCO bulk sample (a) and thick film (b).

Through comparing the data of the X-ray diffraction of standard YBCO powder and the experimental results, it was confirmed that the YBCO thick film has the almost same pattern with sintered YBCO bulk sample.

### 2.4 SEM and optical microscope observation

After the heat treatment procedure, the surface and cross section of YBCO thick film samples were observed by SEM and optical microscope. By the optical microscope observation, cracks on the YBCO layer were found when the content of $BaF_2$ was lower than 2 wt.%. When the content of $BaF_2$ was higher than 2 wt.%, for example, 2, 3 wt.%, no cracks were found on YBCO thick film samples. The Fig.2 shows the surface of $BaF_2$-enriched YBCO thick film wire deposited on Ag and the cross section with thickness about 70 ㎛ thick of YBCO plate deposited on $Al_2O_3$ substrate. The Fig.2 (f) shows double coated YBCO thick film which was deposited on the area of 1st coated layer with lot of cracks on film surface after sintering. The 2nd coated layer was formed to prevent crack surface, which could be occurred after sintering process of 1st coated layer. With this double coating method, cracks on 1st coated layer could be removed by this way.

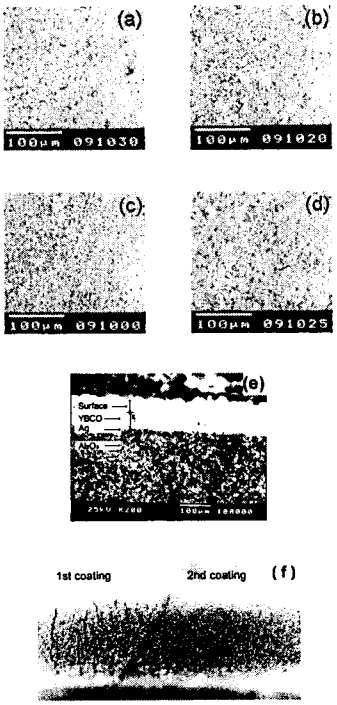
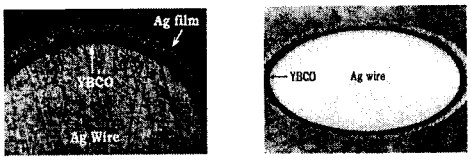



Fig.2. Surface SEM micro-graphs of (a) 0, (b) 1, (c) 2, (d) 3 wt.% $BaF_2$-enriched YBCO wire and (e) cross section view of YBCO plate, (f) surface micro-graph of double deposited wire surface.

Therefore, it was prepared successfully by this double coating method on Ag wire. Silver clading was formed on YBCO thick film by same EPD method. The thick film wire formed by this process was showed in Fig.3 (a) and (b) with partial cross section and angle cut cross section views of single layered wire. It can be seen that

the YBCO thick film and Ag clad was firmly contacted on Ag substrate wire without cracks.




(a) (b)

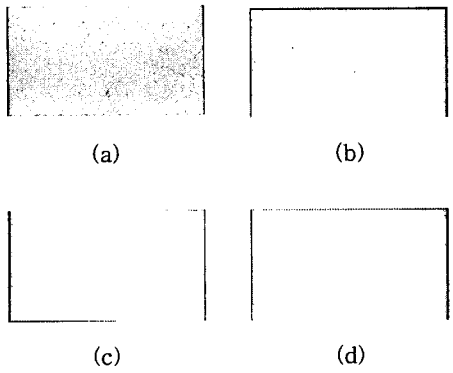
Fig.3. The partial and entire cross section of YBCO wire sample (optical micro-graph)
(a) partial cross section
(b) angle cut cross section

Instead of $BaF_2$, a nonionic polymeric, such as poly(ethylene glycol) (PEG) was used as a new binder. 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.[10)]

The influence of PEG on the viscosity of the suspension, on the compact behavior of HTS powders, and on the strength of as-formed green bodies, as well as the tendency of PEG to migrate during the drying process, have been the subject of several studies. This study has been designed to investigate the adsorption of PEG in colloidal superconducting powder during electrophoretic deposition and then during the drying process.

The adsorption behavior of neutral polymers, such as PEG, as solid surfaces is controlled mainly by the degree of polymerization, polymer concentration in solution, solvency, and net adsorption energy. In this study, a commercially available, almost fully hydrolyzed PEG of moderate molecular weight (6,000) was used. It was applied without further fraction.In practical application, the binder addition is usually in the range of 0 to 3 wt.% (1-10 g/l).

Binder migration during drying is caused by a combined process: transport of PEG by the solvent to the surface during the constant-rate period of the drying process and diffusion of the polymer in the opposite direction due to the developing concentration gradieny. The solvent vaporizes at the surface. However, the nonvolatile PEG remains and, with time, forms a hard surface layer. Since the polymer film is a plastic or viscoelastic solid, its tendency to crack during drying and firing is substantially reduced. By this method, thick HTS films up to 50 $\mu m$ thickness have been made. The solution with a cross-linking agent loses weight gradually and a crack-free film can be easily obtained. Homogeneously distributed 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. In our case we used for 50 ml of suspention 0-0.3 wt.% of PEG. As increasing with PEG, the surface state of wire was densified and crack was decreased. Fig. 4 was shown the surface state of samples.



(a) (b)

(c) (d)

Fig.4. Surface SEM micro-graphs of (a) 0, (b) 0.1, (c) 0.2, (d) 0.3 wt.% PEG-enriched YBCO wire.

### 2.5 Superconductivity and current density

The critical current density, $J_c$ was determined by the standard four-probe method and it was plotted in Fig.5. The transition temperature of the YBCO wire samples were 96 K ($T_{c,onset}$) and 91 K ($T_{c,zero}$), respectively. The critical current densities were 1,215 A/cm$^2$ (2 wt.%); 1,458 A/cm$^2$ (3 wt.%) and 1,921 A/cm$^2$ (bulk), respectively. Those were calculated using measured value of critical current at the point of 1 V criterion of the superconductivity for the $BaF_2$-enriched YBCO wires of 2 wt.% and 3 wt.%, and bulk superconductor.

However, the shape of the I-V curves in Fig.5 (b) and (c) were not same as that of (a). It means

that something of differences were there between bulk and thick film samples, but it is not analyzed in this research.

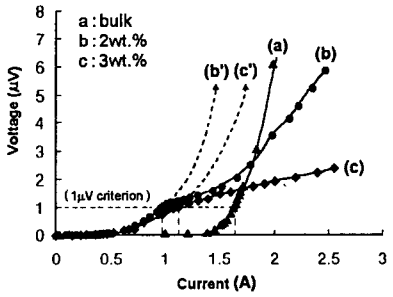



Fig.5. I-V curves of YBCO bulk and thick film wire samples (at 77 K, 0T).

### 3. Conclusion

The YBCO thick film wire and tape could be also prepared well enough by EPD. The suitable conditions and processes for preparing thick film wires/tapes and oxygen absorption heat treatment were obtained successfully in research.

(1) The optimum conditions obtained for preparing YBCO thick films were as follows: 200 mg/l of iodine content, 300-500 V of applied voltage, 10-20 g/l of YBCO powder content in acetone suspension.

(2) After heat treatment of oxygen absorption, the YBCO thick film and bulk samples were well enough with Meissner effect, and the $T_{c,zero}$ was 91 K.

(3) As increasing with PEG, the surface state of wire was densified and crack was decreased.

(4) By the electrophoretic deposition method, the YBCO superconducting wire and tape could be obtained successfully, and the critical current densities, $J_c$ were obtained more than $10^3$ A/cm$^2$ for the prepared YBCO samples.

However, if the thick films with fine YBCO powder could be obtained with uni-axially oriented texturing by EPD, the critical current density, $J_c$ would be sufficiently increased with more than $10^4$-$10^5$ A/cm$^2$ on the Ag based superconductor wire. We are very interested in our future research of rotating electric field assisted EPD process for making oriented and textured superconducting wire.[9]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### References


1. Korea electric research institute (KERI) "Development of new fabrication process and coil application technology for superconducting wires". Final report, 1998.
2. J. G. Bednorz and K. A Muller. J. Phys. B. Vol. 64, 1986. P. 189-94.
3. H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano. Jpn. J. Appl. Phys. Vol. 27, 1988. P. 209-214.
4. Soh Deawha, N. Korobova. Alumina oxide film using electrophoresis. J. of the Research Institute of Industrial Technology. Myongji University. Vol.16, 1997. P.380-382.
5. N. Korobova, Soh Deawha. Electronic materials from alkoxides. Proceedings of the International Conf. of Science and Technology in Kazakstan. Vol. 5, 1997. P. 270-272.
6. Nobuyuki Koura et al. BSCCO superconductor coating by the electrophoretic deposition method. Physica C . Vol.200, 1992. P. 50-54.
7. Deawha Soh, N. Korobova, G. Ksandopoulo, Z. Mansurov. Superconductor thick film wire by electrophoresis method. Proceed. of II Beremjanov Conf. On Chemistry and Chemical Technology. J. Vestnik KazGU. N5, 1999. P. 31-35.
8. S. Cho et al. Jc enhancement of electrophoretic -ally deposited YBCO superconducting wire by $BaF_2$ addition. Appl. Phys. Lett. Vol. 67, N 6, 1995. P. 851-853.
9. Cheng-Feng J. et al. Fabrication of Ag-sheathed Bi-Sr-Ca-Cu-O thick films by a novel a.c.-field assisted electrophoretic deposition method. Physics C. Vol. 314, 1999. P. 291-2.