

# Preparation of Non-cracking YBCO Films Using Electrophoretic Deposition

Deawha Soh\*, Natalya Korobova\*\*

\*Myongji University, Korea, \*\*Kazakh National University, Kazakhstan,  
dwhsoh@mju.ac.kr

*Abstract*— Electrophoretic deposition (EPD) of alcohol YBCO suspensions on the Ag wire electrode was studied. Poly(ethylene glycol) was coordinated to a structure formed by the EPD process with YBCO particles. The suspension is characterized in terms of zeta potential and conductivity. The d.c electric fields of 200-300V/cm are applied for 1-10 min. The optimal condition for the EPD allows modifying the properties and microstructure of the deposited films. Superconducting coatings with nanometer-sized pores and a preferred orientation along the c-axis were prepared from the result with chemically modified precursor solution. In contrast, YBCO coatings of sub-micrometer sized pores and randomly orientated grains were prepared from the solution without PEG.

## I. INTRODUCTION

Since the discovery of high- $T_c$  oxide superconductors, many efforts have been made to develop the practical application of these new materials [1-2]. Most applications require both sufficiently high critical current and ductility. There are so many methods for fabricating wires and tapes and each method has its own advantages and drawbacks. Consequently, the development of bulk devices using high- $T_c$  superconductors seems to remain quite far away. In this context, the fabrication of wires by electrophoretic deposition technique can be considered as one of the convenient methods.

Electrophoretic deposition (EPD) is a powerful method for the production of both thin and thick films [3-5]. EPD process allows production of dense coatings over a conducting material with a good thickness control and complex shape. In EPD charged particles migrate to an electrode of opposite charge under d.c electrical field. The suspension must have a high stability, which can be achieved electrostatically or by adding charged surfactants [6]. After the motion of particles by electrophoresis, a second process, the deposition takes place. According to this, the EPD process requires the control of the suspension properties as well as the selection of the electrical parameters involved during forming. The deposition rate depends on the zeta potential but the ionic flow crossing a surface increases when the charge by unit of weight decreases. This makes it a necessary to arrive at a compromise in such a way that the deflocculates concentration must be as low as possible to minimize the ionic charge, but assuring that the suspension is stable enough to avoid sedimentation [7].

In superconductor application of electrophoresis the composition of the suspension is of great importance. The desired properties of the suspension vehicle are low viscosity, high dielectric constant and low conductivity. Organic liquids have been preferred due to their higher density, good chemical stability and low conductivity.

The major problems associated with the use of organics are that higher voltages are required and their toxic nature and health hazards may require special handling.

Usually the limited thickness for crack-free films is less than 2  $\mu\text{m}$  for the single-layer samples. Thicker single layer mainly makes unexpected crack as a result of the volume shrinkage on the thermal expansion mismatches between film and substrate.

In order to obtain non-porous films, the void in the film should be eliminated. We thus tried to fill up those voids with polymers. The present study concerns the roles of an organic polymer as a chemical modifier in the precursor for coating formation. The roles of poly(ethylene glycol) in YBCO system will be discussed on the pore size, shape, effects connectivity and crystallite size as well as crystallographic orientation of superconducting coatings.

In this investigation, attempts have been made to prepare the quality of the films such as the microstructure, uniformity, critical current density ( $J_c$ ) etc. were improved, using electrophoretic deposition of YBCO together with polymer binder. The aim of this work was to study the parameters of EPD onto silver wire electrode in alcohol YBCO suspensions. The suspension properties have been studied and correlated with the imposed electrical conditions, which strongly depend on them. The suspension requirements for obtaining a deposit, as well as the selection of electrical conditions to enhance the properties of the deposited superconducting films have been studied and interrelated.

## II. Experiment

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder was synthesized with raw materials ( $\text{Y}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{CuO}$ ) and its mean particle size was in the range of 1-5  $\mu\text{m}$ . The fraction of 1  $\mu\text{m}$  is about 10 % and a specific surface area of 4-8  $\text{m}^2/\text{g}$  has been used for deposition. Alcohol suspensions were prepared with a solid content of 0.1-0.2 wt % using ultra-

sonic mixer for 3-5 min. The stability of the suspension was studied by adding different concentration of commercial Poly(ethylene glycol) (PEG with molecular weight 600, 1000, 3400, Wako Pure Chemical Industries).

The suspension properties as well as the processing parameters for EPD were studied. Colloidal stability was studied by measuring the zeta potential of suspensions containing different concentrations of the selected PEG. For this measurement a mass transport analyzer was used. In this technique, the electrophoretic mobility is calculated from the difference in weight of a cell, in which a Ag electrode is located, before and after applying a certain d.c voltage for a fixed time. Although the suspension is deflocculated with a polymer, which can be adsorbed onto the particle surface, the measurement of the zeta potential can give some qualitative idea about the best dispersing conditions.

The EPD experiments were performed using a power supply (Yusung Co., mod. 550A, Korea), which can operate at both constant voltage and constant current. In this work all the experiments were performed maintaining constant voltage.

The electrolytic cell is a glass beaker containing the electrodes and suspension. The counter-electrode consists of a round form grid of Pt and the working electrode is  $\phi 0.8$  mm in diameter of Ag wire (Fig. 1).

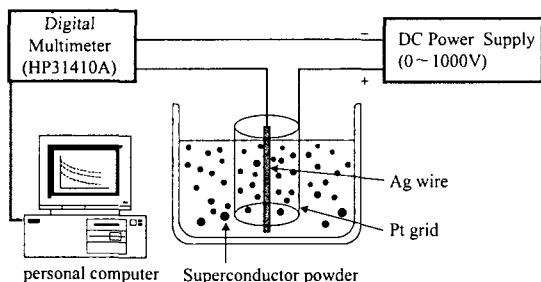


Fig.1. Schematic diagram of electrophoretic system for wire deposition.

The electrodes are assembled to a micrometric screw and maintained at a constant distance of 1.5 cm. This device assures the geometry and hence the reproducibility of the process. The suspensions were stirred with a magnetic stirrer at low speed to avoid turbulence during the deposition process. During the deposition process the particles with positive charges migrate towards the substrate (the cathode) and deposit eventually on it. The current in the beginning of the deposition sharply increase and then after several seconds it starts to drop down slowly.

The thickness of the deposits obtained in the green state was determined with a Digimatic Indicator (Mitutoyo, with accuracy  $\pm 5 \mu\text{m}$ ). After the deposition procedure, the as-deposited films are subjected to a further heat treatment to achieve more a larger content of the superconducting phase and to improve the superconducting properties. The deposits were dried in air, the green densities were measured by Hg immersion, but a high dispersion was obtained due to the low weight

of the deposits. YBCO deposits processed at different conditions were sintered in an electric furnace at 920-930 °C for 1-8 h and then cooled down to 400 °C at a rate of 100 °C/h. At this temperature they were annealed for 0.5 h. After lowering below 200 °C in the furnace, they were taken out of the furnace. During heating and cooling in the furnace, pure O<sub>2</sub> gas was supplied at a rate of 0.5 l/min in controlled the atmosphere of the furnace.

Morphologies of the calcined and sintered films were examined with a scanning electron microscope (SEM) (Hitachi Manufacturing Co., model S-800). EPD coatings were analyzed by Fourier transform infrared spectroscopy (FT-IR) (Micro-20, JASCO, Tokyo, Japan) to investigate the coordination of poly(ethylene glycol) to the YBCO particles. FT-IR analysis was performed using the KBr method. Characteristic absorption peaks were identified by using the N. B. Colthup table (American Cyanamid Co. and Journal of the Optical Society). X-ray diffraction (XRD) of coatings was performed with a Rigaku Denki model RU-300 X-ray diffractometer using CuK $\alpha$  radiation.

Resistivity of the films heated at different temperatures were measured by a d.c 4-probe method using an indium metal electrode with a current of 1 mA. The zero resistivity temperatures were determined by the criterion of 0.1  $\mu\text{V}$ .

### III. Results and Discussion

#### 3.1. Suspension properties

Fig. 2 shows FT-IR spectra of PEG and suspension powders prepared from solution of the YBCO system, organic solution and PEG addition between 1,500 and 1,000  $\text{cm}^{-1}$ . Using triangles in Fig.2 indicates the absorption peaks of PEG.

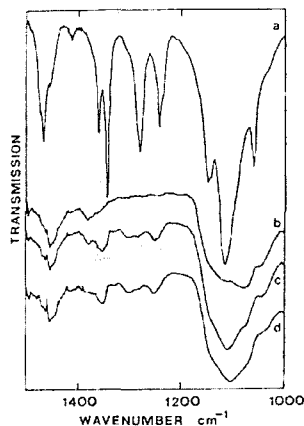


Fig.2. FT-IR of PEG (a); and YBCO powders prepared in iso-propanol suspension without PEG (b), with PEG (c); in mix (iso-BuOH + iso-PrOH) suspension with PEG (d).

The absorption peak at 1466  $\text{cm}^{-1}$  in the PEG spectrum (Fig. 2a) is caused by the bending vibration of the C-H

bond of the  $-CH_2-$  group. The absorption peaks at 1359, 1343, 1280, 1240, 1149 and  $1077\text{ cm}^{-1}$  result from the bending vibration of the O-H bond and the stretching vibration of the C-O bond of the  $-CH_2-OH$  group. The absorption peak at  $114\text{ cm}^{-1}$  is attributed to the  $-CH_2-O-CH_2-$  group.

In the spectrum of the powder in the EPD coating prepared in iso-propanol suspension without PEG (Fig.2b), the absorption peaks at  $1450$  and  $1377\text{ cm}^{-1}$  are from the bending vibration of the C-H bond of the  $-CH_3$  group. In the spectrum of the YBCO powders prepared in iso-propanol suspension with PEG (Fig.2c), the peaks at  $1350$ ,  $1300$  and  $1250\text{ cm}^{-1}$  are new and the band at  $1108\text{ cm}^{-1}$  is broader than those of both PEG and YBCO coatings prepared from iso-propanol suspension without PEG. The new peaks can result from changes of the bending vibration mode of the O-H bond and the stretching vibration mode of the C-O bond of the  $-CH_2-OH$  group, due to bonds such as  $CH_2-O$ .

YBCO was formed between the end  $-OH$  groups of PEG and YBCO particles in organic medium. The broadening of the  $1108\text{ cm}^{-1}$  band can be attributed to the change of the vibration mode of the  $-CH_2-O-CH_2-$  group, which is caused by the formation of bonds between metal and oxygen atoms at the bridging sites of the PEG. Note that the characteristic absorption peaks (indicated by triangles) attributed to PEG appeared in the spectrum. Figure 2(d) shows the spectrum of YBCO powders prepared in mix (iso-BuOH + iso-PrOH) suspension with PEG. All of PEG thus reacts with YBCO atoms to form the bond as  $CH_2-O-$  (YBCO) at both end sites and bridging sites.

### 3.2. Suspension characteristics

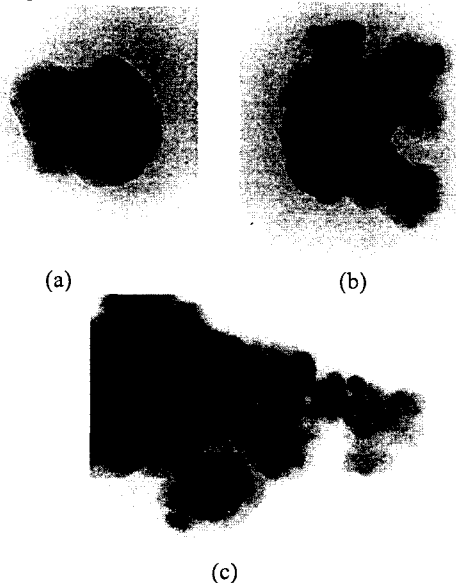


Fig. 3. SEM micrographs of macro-composite particles ("Coated particles") consisting of YBCO cores and various amounts of PEG: (a) separate particles; (b, c) coated aggregated particles moving to Ag electrode during electrophoresis.

The deflocculating curves for a low concentration suspension (such as those required for EPD experiments) have no clear differences, because the viscosity for all prepared suspensions is very low. Thus the viscosity measurements cannot be used as a controlling parameter. The colloidal stability was determined by means of zeta potential measurements. The polymer employed in this work provides an electrostatic stabilization to the suspension (Fig.3).

The zeta potential only gives information about double layer interactions, but does not consider the steric hindrance. However, the zeta potential variation with different PEG concentration in different organic mediums may be used qualitatively for comparison purposes (Fig. 4a,b).

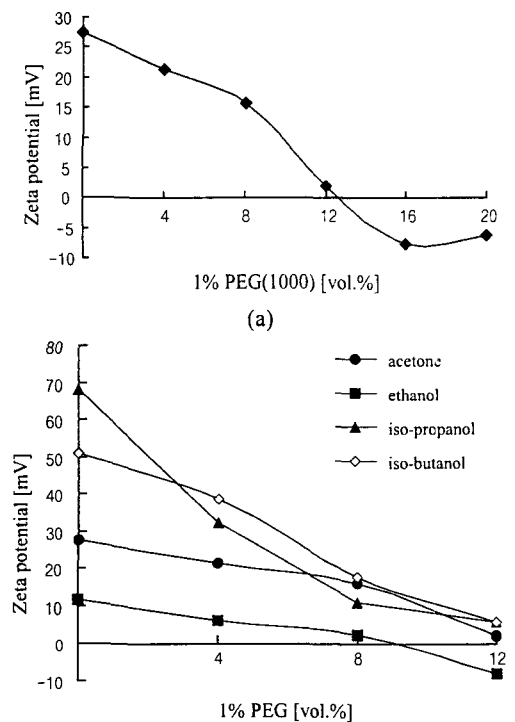


Fig. 4. Zeta potential variation and 1% PEG (1000) contents in organic medium. (a) in acetone suspension; (b) in alcohol suspensions.

The deposit growth will be followed by the current decrease during the current decreases with the increasing deposition thickness, as plotted in Fig. 5. In this picture you can see the difference of YBCO deposition with different content of PEG in the alcohol suspension and its different concentration for applied voltage  $200\text{ V/cm}$ . The curves had an exponential form and became linear after 40 seconds (Fig. 5a) or after 20 seconds (Fig. 5b), because the formation rate was constant until the end of the experiment and the deposition growth did not grow more.

The decrease of the current is due to the depletion of charged particles in the suspension and as a result of the

resistance of the YBCO layer deposited on the cathode [8].

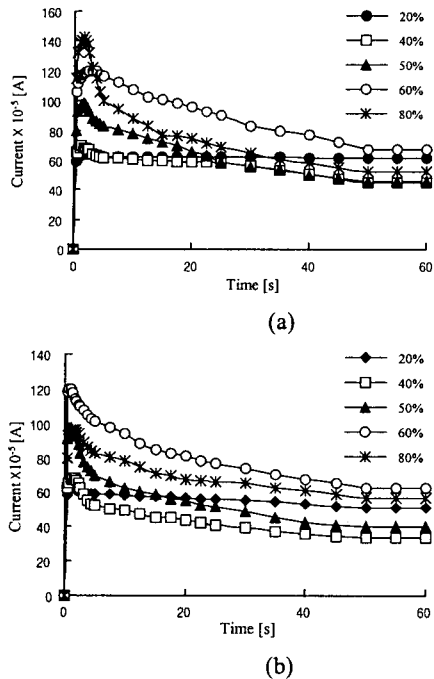


Fig. 5. Current changes vs. deposition time for different iso-C<sub>3</sub>H<sub>7</sub>OH content in the mixing medium of iso-propanol and iso-butanol suspension of YBCO ( 200 V/cm) without (a) and with 1% PEG with 8 vol.% (b).

The green density of the dried samples varies from 53 to 55%. However, these measurements are not reliable because the samples are very thin and brittle and they break easily. Fig.6 shows the thickness of the deposit versus deposition time for alcohol suspension.

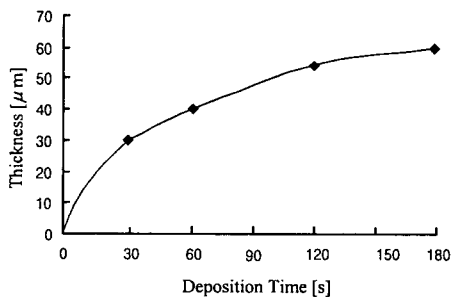


Fig. 6. Thickness of green deposits obtained at different deposition time.

Fig. 7. shows the microstructure of sintered deposits obtained in different suspensions (a) without PEG, with PEG addition (b, c). From the micrographs some significant differences are observed.

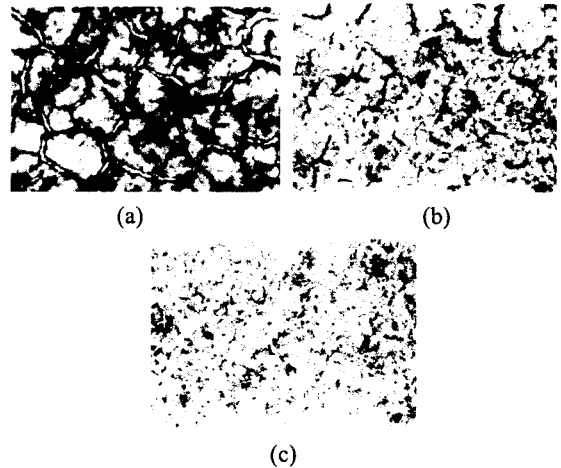


Fig. 7. Micrographs of the YBCO coating microstructure obtained in different suspensions after drying procedure (a) without PEG, with PEG addition (b, c).

In addition, the precursor was used to increase the relative density and to strengthen the films without shrinkage.

It is noted that cracks occur in the calcined film formed by one deposition without PEG if the film thickness exceeds about 2  $\mu\text{m}$ , with PEG exceeds 20-25  $\mu\text{m}$ .

One of the purposes of the current work is to determine the infiltration kinetics of electrophoretic films, formed with a well textured YBCO powder, infiltrated with organic solvent plus PEG polymer that pyrolyzes. We think, that the distribution and microstructure of the intruded and pyrolyzed polymer could be easily observed with the scanning electron microscope (SEM). Because preliminary studies showed that powder in films intruded with the PEG precursor cracked during drying, subsequent powder films were first strengthened by forming small necks between touching particles via sintering without shrinkage (via evaporation-condensation). The cracking phenomenon is detailed elsewhere.

Most of the volatile constituents of the electrophoretic coating are normally removed by drying at temperatures of 125-150  $^{\circ}\text{C}$  (Fig. 7), but a large amount of organic binder still remains in the coating. This must be removed at relatively low temperatures to avoid excessive carbonization and retention of carbon until high temperatures, when it may react with the superconducting frit particles [9]. The early part of the firing cycle must, therefore, provide adequate time at low temperature to ensure complete burn-off the organics and many furnace profiles allow a short dwell time at 250-400  $^{\circ}\text{C}$  for this purpose.

During heating, PEG oxidized and decomposed to carbon dioxide. A flow of clean air is also necessary at this stage to ensure rapid oxidation of carbonaceous residues and to prevent organic fumes from entering the high regions of the furnace. Pores were generated by the

elimination of the gas phase from the coatings. Pores measuring several hundreds of nanometers in diameter arose from the combustion of isolated PEG. Conversely, carbon dioxide generated by the oxidation and decomposition of PEG bonded to YBCO diffused to the surface and desorbed from the surface, leaving nanometer-sized spaces between clusters consisting of YBCO oriented grains.

The main function of the polymer binder to the superconducting particles is to form a bond between the superconducting frit and the substrate, the strength and nature of the bond being dependent on the substrate composition and the processing temperature. At the optimum firing temperature the binder addition should melt and react with the substrate to form a strong chemical bond, and also form a semi-continuous network within superconducting powder.

With correct firing procedures (Fig. 8) there should be no reactions between the frit and the organic binders. Any retained carbon could cause reduction of the frit components with the production of carbon monoxide or carbon dioxide gas, which may cause pinhole or bubbling in the coating (Fig. 8a).

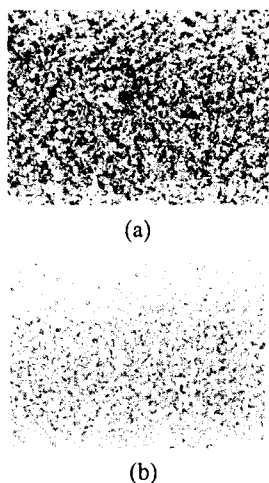


Fig. 8. The surface morphology of pyrolyzed PEG in YBCO electrophoresis films heated at (a) 500 °C; (b) 900 °C in O<sub>2</sub> for 4 h.

The sintered density is high, although a small pore still remains in the compacts, mainly at the triple points and within the grains. The pore size distribution even approaches monodispersity. The electrophoresis parking of particles on the electrode creates extremely regular, narrow channels that may serve as electronics junctions. The close parking of the particles has also been reported to form uniformly close-packed structures, due to capillary forces [7]. PEG with YBCO particles upon pyrolysis of the polymer at elevated temperatures, formed close-packed structures. We suggest that, in this work close packing and ordering phenomena is caused by balanced attractive and repulsive forces, as described by the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [10,11].

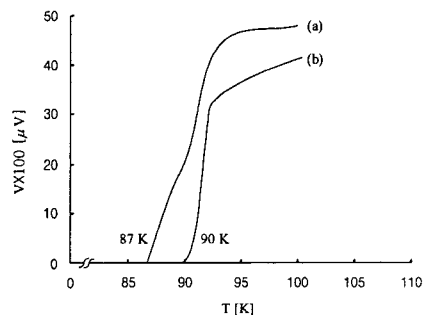
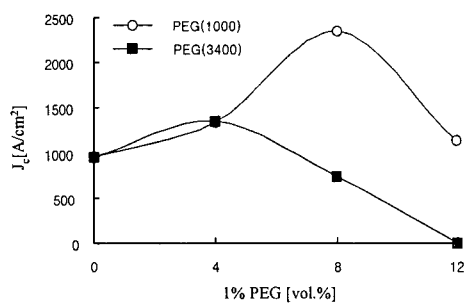
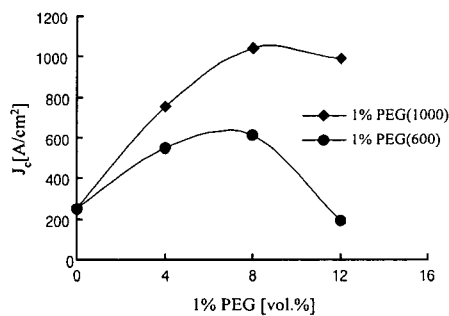


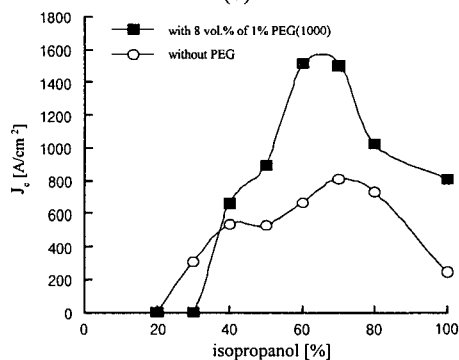
Fig.9. Resistivity-temperature curves of coating films heated at 920 °C for 1h. The thickness of the film is about 30 μm for (a) and about 25 μm for (b) with PEG.



(a)



(b)



(c)

Fig.10. The influence of PEG concentration and its molecular weight on the critical current density: (a) in acetone suspension; (b) iso-propanol suspension; (c) in mix (iso-BuOH + iso-PrOH) suspension.

The DLVO theory has been invoked earlier to explain ordering observed in films of concentrated suspensions of latex and gold particles [12]. The Stern layer, the compact layer of the ions immobilized on the colloidal surface, will be larger and more polarizable for suspension without PEG (Fig. 3). We suggest that optimal concentration of polymer leads to a decrease rate of flocculation and agglomeration of the colloidal particles during film formation, leading to ordered films. This suggestion has been tested by varying the PEG concentration, and also by varying the dielectric constant of the colloidal medium, and both have shown to result in ordered and close-packed structures.

Resistivity-temperature curves of the films heated at 920 °C for 1h are shown in Fig. 9. The fabricated thick film showed uniform surface morphology with less voids and cracks. It is shown that the 25 μm thick film is superconductor, exhibiting a complete resistivity drop to zero at 90 K, although it is semiconductor like at high temperatures.

When subjected to PEG treatment, the 25 μm thicker film is metallic at high temperatures and shows a sharp resistivity drop at 90 K, becoming a superconductor with  $T_{c0}$  of 89 K.

#### IV. Conclusion

The quality of the samples prepared by electrophoretic deposition technique has been closely studied. The effect of several factors on the EPD deposition of YBCO films with and without PEG has been studied. The density of the coatings as well as the resultant microstructure can be significantly improved by employing polymer binder (PEG). The morphological and electrical properties of the YBCO films have been discussed. The maximum  $J_c$  obtained is ~2500 A/cm<sup>2</sup> at 25 μm thick film with PEG addition in suspension. EPD deposition technique is suitable to coat large complex shaped objects and may find its early application in microwave technology.

#### REFERENCES

- [1] Bednorz J.G., Muller K.A., New high- $T_c$  superconductors, *Z. Phys. B*, Vol. 64, 1986, pp.189-193.
- [2] Soh D., Li Y., Park J., Cho Y., Preparation of superconducting YBCO thick film by electrophoresis, *Physica C*, Vol. 337, No. 1-4, 2000, pp. 44-48.
- [3] Abolmaali S.B., Talbot J.B., Synthesis of superconductive thin films of  $YBa_2Cu_3O_{7-x}$  by a non-aqueous electrodeposition process, *J. Electrochem. Soc.*, Vol. 140, N 2, 1992, pp. 443-445.
- [4] Hein M., Muller G., Piel H., et al., Electrophoretic deposition of textured  $YBa_2Cu_3O_{7-x}$  films on silver substrates, *J. Appl. Phys.*, Vol. 66, N 12, 1989, pp. 5940-5943.
- [5] Schmid T.E., Wolter H., Organically modified ceramics and their applications. *J. Non-Cryst. Solids*, Vol. 121, 1990, pp. 428-435.
- [6] Korobova N., Soh D., Jeon Y., Li Y., Lim B., Improvement on Deposition Density of Electrophoretic Superconducting Thick Film, *Journal of the Research Institute of Industrial Technology (Korea)*, Vol. 20, 2001, pp.489-492.
- [7] Sarkar P., Nicholson P.S., Electrophoretic deposition (EPD): mechanisms, kinetics, and application to ceramics, *J. Am. Ceram. Soc.*, Vol. 70, No8, 1996, pp. 1987-2002.
- [8] Soh D., Korobova N., Ksandopulo G., Mansurov Z., "Superconductor thick film wire by electrophoresis method", *Proc. of II Beremjanov Conf. on Chemistry & Chemical Technology*, 1999, Almaty, Bull. KSNU, Vol. 17, N5, pp.31-35.
- [9] Soh Deawha, Korobova N., Fan Zhanguo, Moisture corrosion and surface protection of YBCO superconductors, II Intern. Symposium "Physics & Chemistry of Carbon Materials", Kazakhstan, Almaty, 19-20 Sept. 2002, pp.33-36
- [10] Deriaguin B., Landau L., Theory of stability of highly charged lyophobic sols and adhesion of highly charged particles in solutions of electrolytes, *Acta Physicochim.*, USSR, Vol. 14, 1941, p. 633-52.
- [11] Verwey E., Overbeek J., Theory of stability of lyophobic colloid, Elsevier, Amsterdam, The Netherlands, 1948.
- [12] Kumar K.N., Keizer K., Burggraaf A.J., Okubo T., Nagamoto H., Morooka S., *Nature*, Vol. 358, 1992, pp. 48-50