

Preparation of Crack-free YBCO Films by EPD on Silver

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Abstract—Electrophoretic deposition (EPD) of alcohol YBCO suspensions on the Ag wire electrode is 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 200-300 V/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 submicrometer-sized pores and randomly orientated grains were prepared from the solution without PEG.

Index Terms—Electrophoretic deposition (EPD), Poly(ethylene glycol), Suspension, Crack-free, YBCO

I. INTRODUCTION

Since the discovery of high- T_c oxide superconductor, 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 superconductor 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]. EPD process allows production of dense coatings over a conducting material with a good thickness control and complex shape.

II. Al_2O_3 FORMATION BY ANODIZING METHOD

$YBa_2Cu_3O_{7-x}$ powder was synthesized with raw materials (Y_2O_3 , BaO, CuO) and its mean particle size

was in the range of 1-5 μm . The fraction of 1 μm is about 10 % and a specific surface area of 4-8 m^2/g has been used for deposition. Alcohol suspensions were prepared with a solid content of 0.1-0.2 wt% using ultrasonic 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. 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 0.8 mm in diameter of Ag wire (Fig. 1). Morphology of the calcined and sintered films were examined with a scanning electron microscope (SEM) (Hitachi Manufacturing Co., model S-800). Resistivities 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 V.

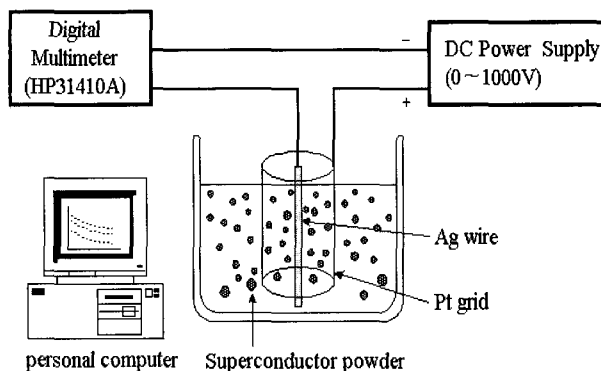


Fig. 1 Schematic diagram of electrophoretic system for powder deposition.

III. RESULTS AND DISCUSSION

The deflocculating curves for a low concentration suspension (such as those required for EPD experiments) has 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. 2).

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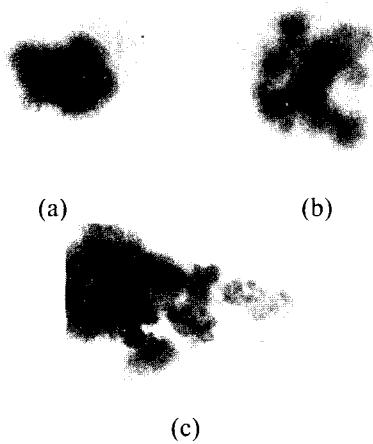


Fig. 2 SEM micrographs of macro-composite particles (coated particles) consisting of YBCO cores and various amounts of PEG: (a) separate particle, (b), (c) aggregated particles moving to Ag electrode during electrophoresis..

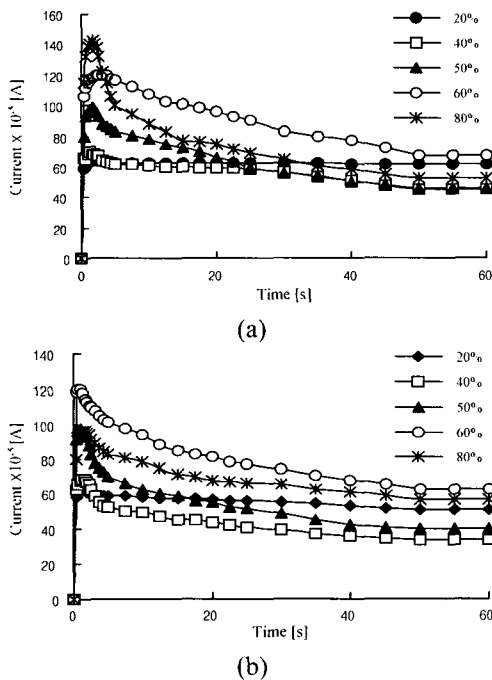


Fig. 3 Current changes vs. deposition time for different iso-C₃H₇OH content in the mixing medium of iso-propanol and iso-butanol suspension of YBCO (200 V/cm) without (a) and with 1% PEG of 8 vol.% (b).

The deposit growth will be followed by the current decrease during the increasing of deposition thickness, as plotted in Fig. 3. 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 V/cm. The curves had an exponential form and became linear after 40 seconds (Fig. 3a) or after 20 seconds (Fig. 3b), 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 [6].

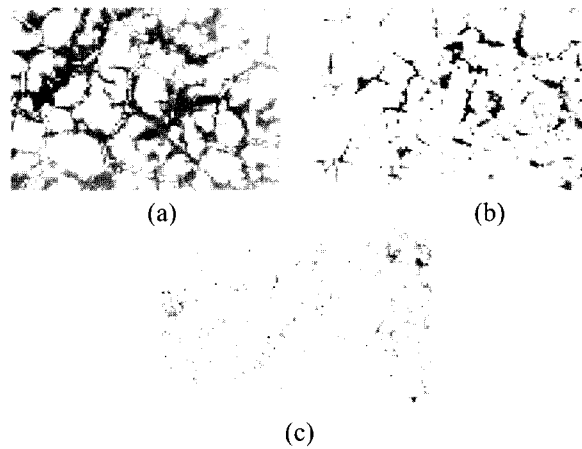


Fig. 4. Micrographs of the YBCO coating microstructure obtained in different suspensions after drying procedure (a) without PEG, with PEG addition (b,c).

Fig. 4. shows the micro-structure of sintered deposits obtained in different suspensions (a) without PEG, with PEG addition (b, c). From the micrographs some significant differences are observed. 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 μm , with PEG exceeds 20-25 μm . One of the purpose 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 to be pyrolysis. We think, that the distribution and microstructure of the intruded and being pyrolysis 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. 4), 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 [5]. 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 nanometer 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. 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 mono-dispersive. The electrophoresis parking of particles on the electrode creates extremely regular, narrow channels that may serve as electronics junctions. 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 [6,7]. The DLVO theory has been invoked earlier to explain ordering observed in films of concentrated suspensions of latex and gold particles. 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. 2). 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. 5.

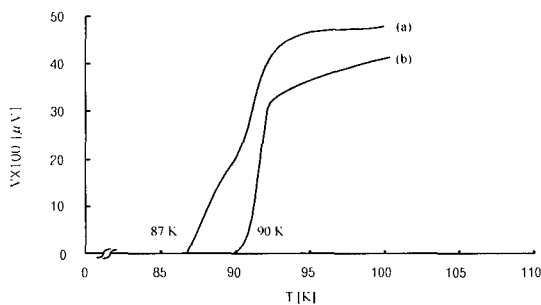


Fig. 5 Resistivity-temperature curves of coating films heated at 920 °C for 1h. The thickness of the film is $\sim 30 \mu\text{m}$ for (a) and $\sim 25 \mu\text{m}$ for (b) with PEG.

The fabricated thin film showed uniform surface morphology with less voids and cracks. It is shown that the $25 \mu\text{m}$ thick film is superconducting, exhibiting a complete resistivity drop to zero at 90 K, although it is semiconducting at high temperatures. When subjected to PEG treatment, the $25 \mu\text{m}$ 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.

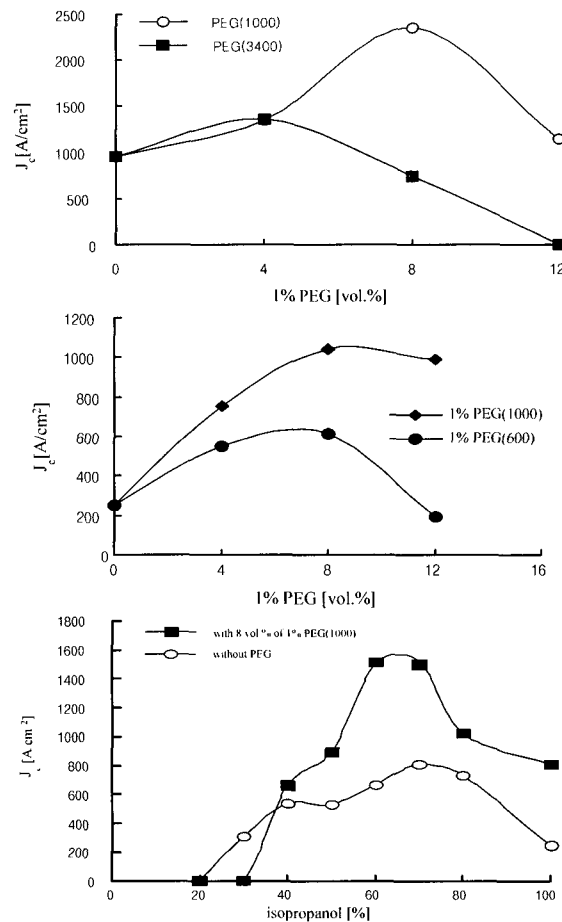


Fig. 6 The influence of PEG concentration and its molecular weight on the critical current density : (a) in acetone suspension; (b) isopropanol suspension; (c) in mix (iso-BuOH + iso-PrOH) suspension.

We think that the presence of large disorientation between grains creates an array of weak links with a dispersion of their critical currents. The critical current density J_c was also associated with the anisotropy of YBCO films. So, in our future work we will investigate the preferential orientation during EPD with using magnetic field during the deposition process. Superconducting properties measurement on these films is very promising.

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 $\sim 2500 \text{ A/cm}^2$ at $25 \mu\text{m}$ 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.

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REFERENCES

- [1] Bednorz J.G., Muller K.A., New high- T_c superconductors, *J. Phys.*, Vol. 64, p.189, 1986
- [2] Soh D., Li Y., Park J., Cho Y., Preparation of superconducting YBCO thick film by electrophoresis, *Physica C*, Vol. 337, No. 1-4, p. 44, 2000
- [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, No. 2, p. 443, 1992
- [4] Soh D., Korobova N., Ksandopulo G., Mansurov Z., Superconductor thick film wire by electrophoresis method, Proc. of II Beremjanov Conf. on Chemistry & Chemical Technology, Almaty, Bull. KSNU, Vol. 17, No. 5, p.31, 1999
- [5] 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. p. 33, 2002
- [6] Deriaguin B., Landau L., Theory of stability of highly charged lyophobic sols and adhesion of highly charged particles in solutions of electrolytes, *Acta Physicochem.*, USSR, Vol. 14, p, 633, 1941
- [7] Verwey E., Overbeek J., Theory of stability of lyophobic colloid, Elsevier, Amsterdam, The Netherlands, 1948.



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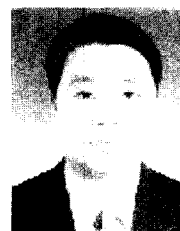


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