

Preparation of Crack-free HTS YBCO Films by EPD Method

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Electrophoretic deposition (EPD) of alcohol YBCO suspensions on the Ag wire electrode is studied. Polyethyleneglycol was coordinated to a structure formed by the EPD process with YBCO particles. 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.

Keywords : EPD, Polyethyleneglycol, Suspension, Crack-free, YBCO

1. 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 (EPD) technique could be considered as one of the convenient methods. The electrophoretic deposition is a powerful method for the production of both thin and thick films[3,4]. EPD process allows production of dense coatings over a conducting material with a good, useful thickness control and complex shape.

In this investigation, attempts have been made to prepare the better quality of the films such as the microstructure, uniformity, critical current density (J_c) etc. were improved, using the electrophoretic deposition method for YBCO thick films together with polymer binder of polyethyleneglycol (PEG).

2. EXPERIMENTAL

$YBa_2Cu_3O_{7-x}$ 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 was 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.

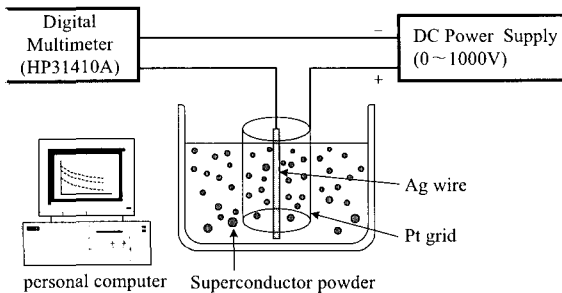


Fig. 1. Schematic diagram of electrophoretic system for powder deposition.

3. RESULTS AND DISCUSSION

Figure 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 cm^{-1} . Using triangles in Fig.2 indicates the absorption peaks of PEG.

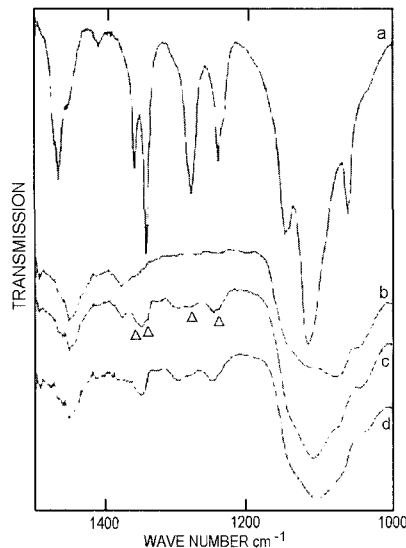


Fig. 2. FT-IR of PEG (a); and YBCO powders prepared in iso-propanol suspension without PEG (b), with PEG (c); in mix (iso-BuOH + iso-PrOH) suspension with PEG (d).

The absorption peak at 1466 cm^{-1} in the PEG spectrum (Fig. 2a) is caused by the bending vibration of the C-H bond of the $-\text{CH}_2-$ group. The absorption peaks at 1359, 1343, 1280, 1240, 1149 and 1077 cm^{-1} result from the bending vibration of the O-H bond and the stretching vibration of

the C-O bond of the $-\text{CH}_2-\text{OH}$ group. The absorption peak at 1140 cm^{-1} is attributed to the $-\text{CH}_2-\text{O}-\text{CH}_2-$ 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 cm^{-1} are from the bending vibration of the C-H bond of the $-\text{CH}_3$ group. In the spectrum of the YBCO powders prepared in iso-propanol suspension with PEG (Fig. 2c), the peaks at 1350 , 1300 and 1250 cm^{-1} are new and the band at 1103 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 $-\text{CH}_2-\text{OH}$ 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 1103 cm^{-1} band can be attributed to the change of the vibration mode of the $-\text{CH}_2-\text{O}-\text{CH}_2-$ 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.

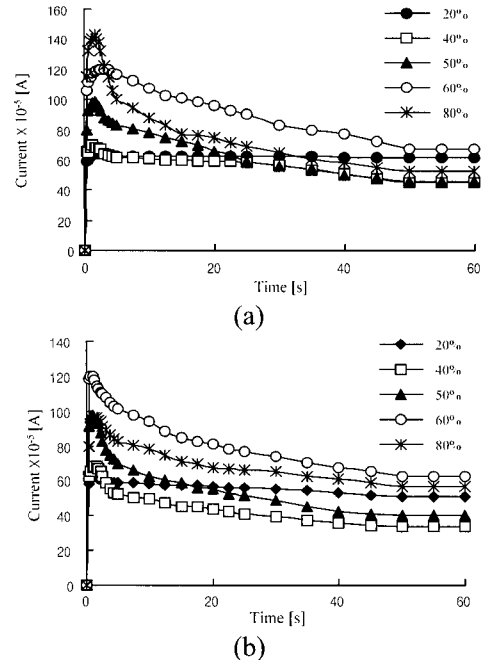


Fig. 3. Current changes vs. deposition time for different iso-propanol content in the mixing medium of iso-propanol and iso-butanol suspension of YBCO (200 V/cm) without (a) and with 1% PEG of 8 vol.% (b).

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 content of 1% PEG of 8 vol.% 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 [5].

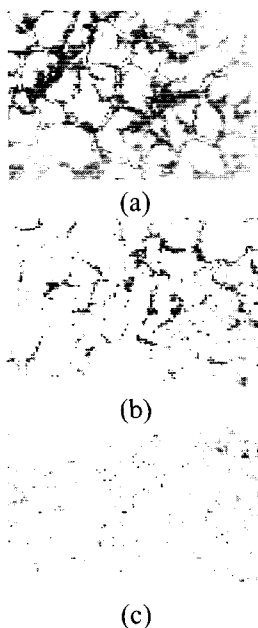


Fig. 4. Micrographs of the YBCO coating microstructure obtained in different suspensions after drying procedure (a) without PEG, with PEG addition (b), (c) ($\times 200$).

Figure 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 $^{\circ}$ 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 [6]. 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 $^{\circ}$ 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[7,8]. 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. 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. 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.

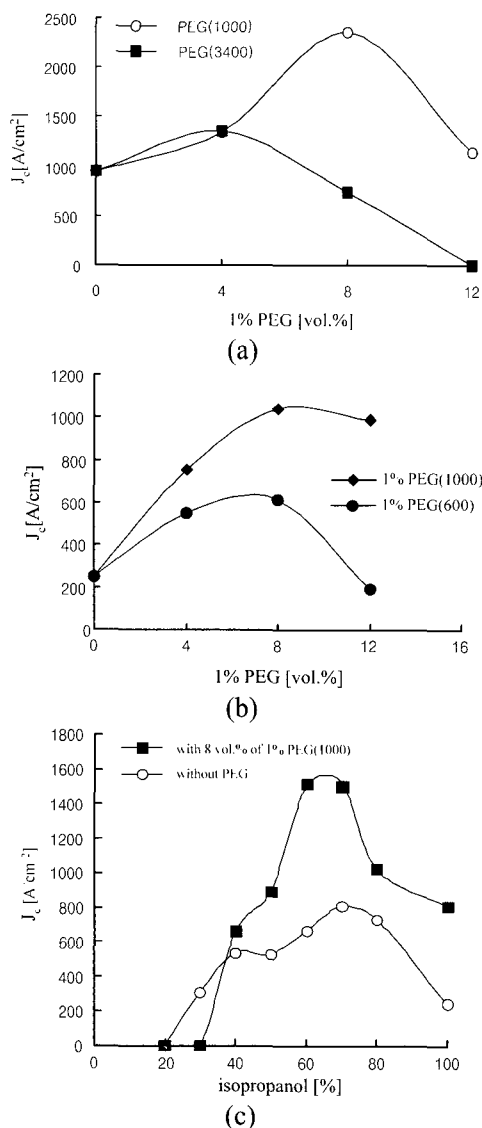


Fig. 5. The influence of PEG concentration and its molecular weight on critical current density: (a) in acetone suspension; (b) iso-propanol suspension; (c) in mix (iso-BuOH + iso-PrOH) suspension.

4. 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/cm² at 25 μ 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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