

The influence of polymer compounds on the HTS films

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Abstract

In this work the results of the systematic investigations on the effect of organic addition by using polymer compound as starting materials on the superconducting properties of YBCO electrophoretic deposited films on silver substrate are presented. The characteristics of the films were examined by X-ray diffraction and SEM observation. Our results show that the adhesion and microstructure of these films are sensitive to the nature of polymer compounds and sintering conditions (electrophoretic deposition, drying and heat-treatment procedures). To develop optimum microstructures for samples processed in this manner it is necessary to have an understanding of how these processes affect the microstructure and hence the properties of ceramic superconductors.

Keywords : Electrophoretic Deposition, Polymer, Polyethylene Glycol, Ethylene Glycol

1. Introduction

The observation of superconductivity above liquid nitrogen temperature in oxide systems has encouraged researchers throughout the world to focus on this field because of the tremendous potential for application of these materials. Many of these applications require the use of superconductors in the forms of wires or strips. A simple and cheap method for the fabrication of superconducting wires is to make a coating on a metallic substrate by electrophoretic deposition followed by appropriate heat treatment. A prominent feature of these films is the presence of cracks. It is, however, important that such films are crack free for many applications. Organic additives are extensively used in colloidal processing of ceramic powders to adjust the forces between the particles in the suspension as well as in the green body [1-2]. We have thus studied the crack formation as a function of weight addition and polymer nature [3]. In this paper, we first experimentally compare the influence of polymer,

nature(PEG : Polyethylene Glycol and EG : Ethylene Glycol), utilizing a variety of suspension media for electrophoretic deposition of YBCO superconductor powder.

2. Experiment

A flow chart for the preparation of a chemically modified precursor solution for HTS coatings is given in Fig.1. YBCO (Wako Pure Chemical Industries, Ltd., Osaka, Japan), ethanol or acetone were mixed and stirred to prepare suspension. The ethanol or acetone concentration of the mixture was 1 wt%. Poly(ethylene glycol) (PEG with molecular weight = 6,000), Wako Pure Chemical Industries was then added to the suspension in the range of 0 to 3 wt. % (1-10 g/L)..

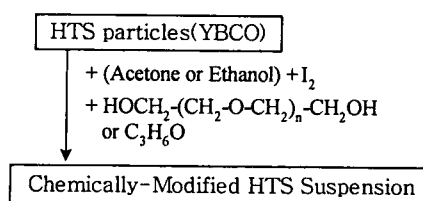


Fig.1. Flow diagrams for the preparation of chemically modified suspension for YBCO coatings.

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YBCO coatings were deposited by electrophoresis method on Ag wire at 150–250 V and 0.25–120s. After the coatings were dried at 100°C, they were heated slowly (at a rate of 2°C/min) up to 950°C in the air. Microstructures of these films were examined by scanning electron microscopy (SEM) (JSM-T200, JEOL, Tokyo, Japan).

3. Results and Discussion

In this work in addition to a HTS ceramic 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. 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, has 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. 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 gradient.

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. We state that, no densification was observed during drying procedure prior to the formation of a liquid phase. During polymer melting the presence of liquid was easily determined either by gross changes in particle shape or the appearance of small pools of

liquid (Fig.2).

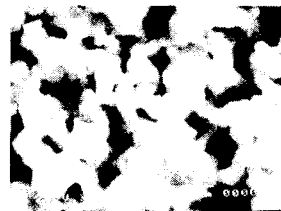


Fig.2. Microstructure of YBCO films with PEG addition after drying procedure at 300°C.

By this method, thick HTS films up to 50 μ m thickness have been made. Homogeneously distributed PEG organics was burned off below 600°C prior to texturing under controlled conditions and the remaining pores were very small and can easily be densified at lower temperature. A SEM image typical of the optimized HTS films is shown in Fig. 3.

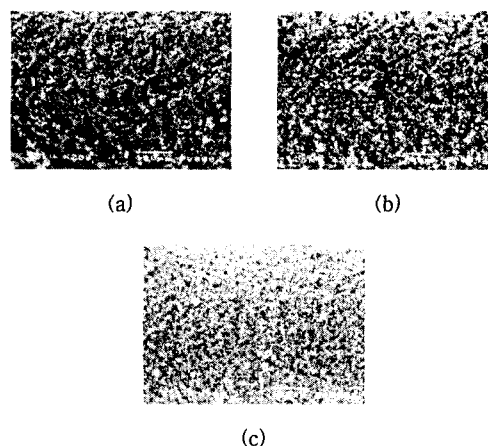


Fig.3. SEM micrographs of YBCO films electrophoresed in acetone suspension with the same conditions : (a) without polymer, (b) with addition of 1ml 1 % PEG, (c) with addition of 3ml 1 % PEG.

The particle-size distribution is narrow (3–5 μ m), with a majority of the particles being \sim 3 μ m. However, the extent of porosity vary 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, is not very clear and warrants

further studies. Scanning electron microscopy photograph of the fractured surface of YBCO films shows the compacts with larger grains of a few micrometers size and smaller submicron grains dispersed. You can see that the grains bonded tightly and the fracture occurred by both transgranular and intergranular modes.

The results show the best films with addition 1% PEG concentration. 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 are shown on Fig.4 for YBCO films as an example of effectiveness of various suspensions media for electrophoretic deposition. Optimum dispersion in ethanol appears at about 3 % PEG concentration and 1ml of additive.

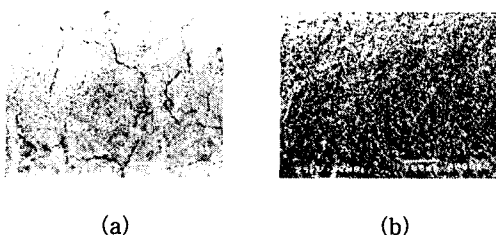


Fig.4. Micrographs for YBCO films in ethanol with 3 % PEG addition: (a) 0ml addition, (b) 1ml.

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. 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 HTS 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.

Polymers can be good dispersants only in suitable solvents. PEG is dissolved completely ethanol is used as the dispersing medium. Under ideal solvency conditions (called θ solvent), polymer molecules of

several thousand molecular weight behave as if they are ideal small molecules. At the point, the polymer segments change from exhibiting a net mutual repulsion to a net mutual attraction. The adsorption of polymer molecules at an interface, which determines the segment density distribution function, is critically dependent upon, any factors, which include (1) the chemical constitution of the polymer, (2) the chemical nature and geometrical shape of the interface, (3) the chemical composition of the solvent, (4) the mode of attachment of the polymer chains to the surface, and (5) the surface density of the polymer molecules at the interface. It is the subtle interaction of these diverse factors that determines the conformation of a polymer at an interface and thus the steric interaction in a particular system. In the present investigation, the electrophoresed YBCO films in ethanol suspension with EG addition have been studied. Based on the SEM results obtained, a mechanism for YBCO particles accumulation on the surface of Ag electrode has been proposed and optimum conditions to prepare dense with minimum cracks film have been identified (Fig.5).

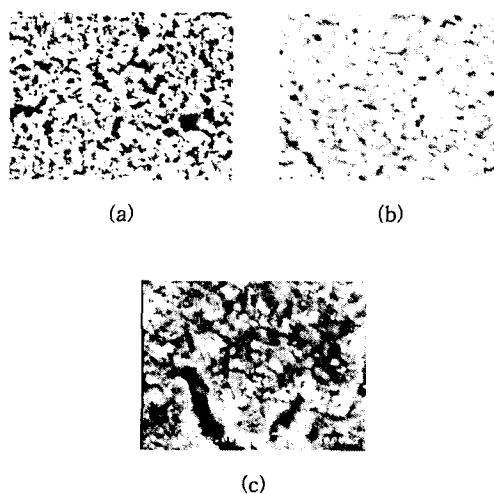


Fig.5. SEM micrographs of YBCO films electrophoresed in acetone suspension with the same voltage and time conditions as in Fig.3: (a) with addition of 0.3 ml EG, (b) with addition of 1ml EG, (c) with addition of 2ml EG.

Because ionic nature solvents are used, problems result. We identified the most serious problem as the formation of hydrogen (cathode) and oxygen (anode), resulting in bubbles in the cast, attack on the electrodes, and local heating in the suspension. Addition of EG to acetone increased the stability of the suspensions, but the coatings were still soft. We also reported [3] that the increasing EG concentration more than 1.0ml produced significant hydrogen and considerable density reduction. In the case of EG addition we suggested an electrochemical mechanism of deposit formation. The basis of our mechanism is the DLVO theory [5-6]; i.e., an increase of EG concentration can induce coagulation of the system. We proposed the deposit forms because of particle flocculation via the increased EG concentration thereabout and the resultant reduced zeta potential near the electrode. A suspension with low zeta potential forms a viscous deposit because such a suspension is not stable; i.e., it forms agglomerates, which under a DC field, move toward the depositing electrode and form a low-density deposit with low strength.

This preliminary report represents the beginning of more extensive studies into the variety of organic additive applications. Many experiments are in progress to decrease the width of the superconducting transition, the morphology of the films, and the application of organic additives.

4. Conclusion

1. Since cross-linking agents are used to form a hybrid polymer solution, when the solvent evaporates the relaxation behavior of the hybrid polymer film can lead to a very dense network and a crack-free YBCO film can be easily obtained.

2. From the resulting chemically modified precursor solution, YBCO coating from acetone consisting of nano meter sized pores and grains with diameters of 1.5-3.0 μ m and a preferred orientation along the c-axis were prepared on the Ag wire by electrophoresis method. In contrast, YBCO coatings consisting of macrosized pores and cracking surfaces were prepared from acetone solution with the ethylene glycol addition.

Acknowledgement

This work was accomplished by KISTEP grant of I-00-042 for int'l joint-research program and '99RU10-015 for exchange scientist program.

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