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Preparation of Y-Ba-Cu-O Superconducting Film on Ag Substrate by an Electrophoretic Deposition Method

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The preparation of $YBa_2Cu_4O_8$ thick film on Ag substrate by electrophoretic deposition was directly studied. Electrophoretic deposition was carried out in solution, which was composed of presintered $YBa_2Cu_4O_8$ powder, sodium, and 2-propanol as a solvent. The deposited thick films were heat-treated in O_2 at 815℃ for 12 hours and at 450℃ for 12 hours. We succeeded in obtaining superconducting $YBa_2Cu_4O_8$ films on Ag substrate. Even though the chemical reactions at the $YBa_2Cu_4O_8$/Ag interface occurred in the range of 10 μm, superconductivity was not depressed. The thickness of the films was in the range of 60-80 μm. The characteristics of the films were examined by electric resistance measurements, X-ray diffraction, and SEM observations.

Introduction

The discovery of the superconductor, Y-Ba-Cu-O[1] system, has led to intensive efforts at developing these ceramics into useful materials. Although a number of fabrication approaches have been studied, its applications were not easy due to the inherent brittleness of ceramic materials and the difficulties in forming the high T_c superconductor into desired shapes.

Thick-film fabrication techniques have been widely investigated because the prospect of coated superconducting materials offers a lot of promising advantages. Techniques such as plasma spraying[2], screen printing[3], and sol-gel method[4] have been utilized to make Y-Ba-Cu-O coatings.

We prepared good superconducting films deposited on Ag substrate using the electrophoretic method[5]. Electrophoretic deposition is an electrokinetic phenomenon in which charged particles suspended in a liquid vehicle are moved and deposited under the influence of an electric field.

This method has several advantages high throwing power, short deposition time and its versatility, etc.

Electrophoric deposition method was used for beta-alumina ceramics[6] and CdSe[5] coating films. Recently, some groups prepared the thin films of $YBa_2Cu_3O_{7-x}$ by this method[7,8]. They used buffer layer or I_2/acetone as electrolyte /solvent. Since the acetone has low boiling point (56℃), it easily boiled during this experiment. In our work, 2-propanol (its boiling point is 82℃) was used as solvent and Na was utilized as electrolyte because I_2 was not dissolved in 2-propanol. Until now, $YBa_2Cu_3O_7$ compounds were only used as the ceramic powders of electrophoretic method because it was difficult to prepare $YBa_2Cu_4O_8$ samples. Lately we had prepared $YBa_2Cu_4O_8$ bulk samples[9] at 1 atm in O_2 condition, therefore, we utilized $YBa_2Cu_4O_8$ samples as starting powders. When buffer layer is not used, interface chemical reaction is crucial. But the heat-treatment temperature of $YBa_2Cu_4O_8$ samples (815℃) is lower than that of $YBa_2Cu_3O_7$ samples (about 915℃). The chemical reaction at the $YBa_2Cu_4O_8$ /Ag interface is less effective on the their properties.

Experiment

Electrophoretic deposition was carried out in solution, which was composed of presintered $YBa_2Cu_4O_8$ ceramic powders (1.5 g), sodium, and 2-propanol (150 m*l*). The sodium was used in order to play electrolyte and to prevent the particle from settling during the deposition time.

Using the pyrolysis method of EDTA complex[9], the stoichiometric amounts of high purity powders $Y(NO_3)_3$, $Ba(NO_3)_2$, and $Cu(NO_3)_2$ were dissolved in purified de-ionized water together with EDTA and converted to metal-oxide powders by pyrolysis, and then $YBa_2Cu_4O_8$ powders were sintered at 815℃ for 48 hours. This process offers the advantage of forming the fine particles to develop a suitable charge on the surface and to produce high densification in sintering process. The powders were ball-milled for 12 hours with

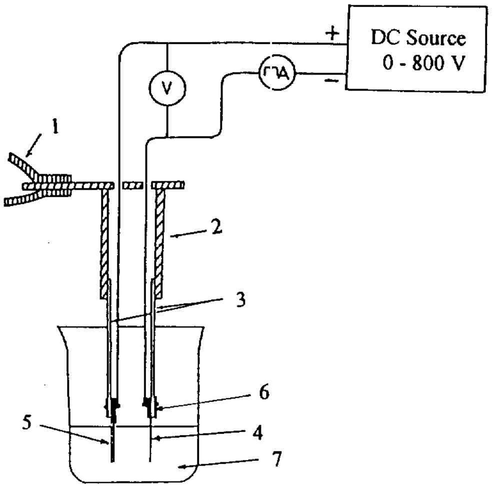

Figure 1. Experimental setup for electrophoretic deposition. 1. Clamp, 2. Plastic plate, 3. Glass plate, 4. Copper plate, 5. Silver anode, 6. Electrode holder, 7. Suspension.

α-alumina grinding media. Our experiments were performed in a 50 m*l* beaker containing about 15 m*l* of suspension as shown in Figure 1. The negative and positive electrodes were silver and copper substrates, respectively. Before the electrophoretic deposition process, a silver substrate was polished with 1 μm-alumina powder to activate the silver substrate surface. The deposited samples were heat-treated at 815℃ for 12 hours, 450℃ for 12 hours in a controlled O_2 atmosphere. We heated (3℃/min) the coated samples slowly, in order to minimize the cracking of the coating. The superconductivities of all the samples were checked by X-ray analysis, SEM, and resistivity-temperature measurements.

Results and Discussion

The electrical conductivity of a number of suspensions is shown in Figure 2, as a function of the dielectric constant of the solvent[5]. The electrophoretic deposits were only obtained from the solvents with dielectric constants in the range from 12 to 25 as indicated by the filled squares on the figure. The solvents such as benzene or ethyl acetate have low dissociating powers, thus they would not give rise to effective particle charging. Despite sufficient charging solvents like methanol and ethylene glycol, their strong interaction between powders and solvents makes the particles aggregate on the electrode. The deposits formed from solvents with dielectric constant slightly below 25 (for example, 2-propanol, acetone) are so fluid that they would slide off from the electrode. All subsequent works were carried out with 2-propanol. Its dielectric constant is 18.

The limitation of the particle charging is that ceramic powder would not be suspended in solution during deposition time. However, the oxidation of sodium metals give rise to a sufficiently charged particle and hydrogen gases from 2-propanol. This is represented by the following reaction;

$$Na(s)+2R_2CHOH \rightarrow Na^+(aq)+2R_2CHO^- + H_2 \quad (R=CH_3)$$

R_2CHO^- develops a surface charge on the ceramic particles, which are fully suspended in solvent during the experiment.

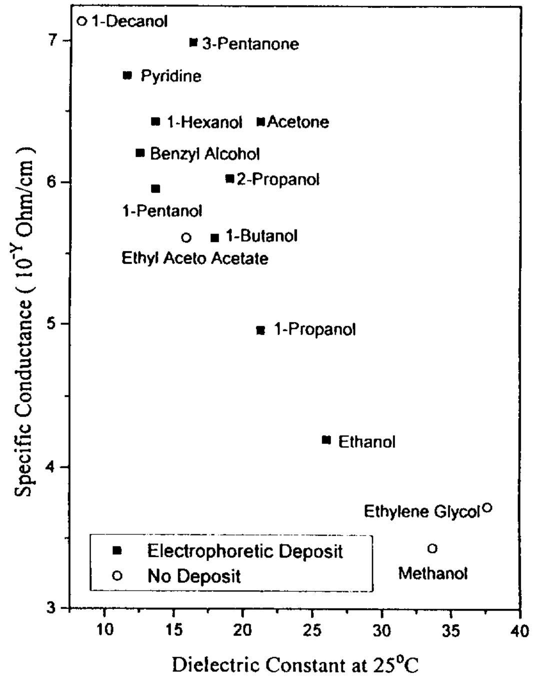

Figure 2. The electrical conductivity of suspensions *vs.* dielectric constant of their vehicles.

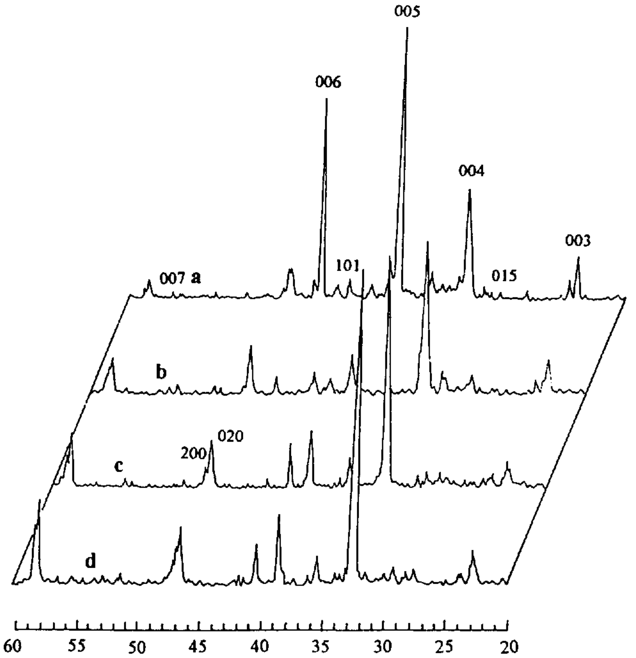

Figure 3. X-ray diffraction pattern of Y-Ba-Cu-O.
a) Na: 100 mg, b) Na: 30 mg, c) Na: 10 mg, d) Bulk sample.

The sodium ion deposited on negative electrode by reduction and mixed with ceramic deposits. It has been known that the substitution of Y^{3+} in YBCO by sodium ion does not much affect the superconducting properties[10]. But, when the amount of sodium is increased, the sodium ion is more easily deposited than partially charged ceramic particle. Since the ionic size of Na^+ is almost identical with that of Y^{3+}, Na^+ is expected to be substituted into Y^{3+} site. In the so-

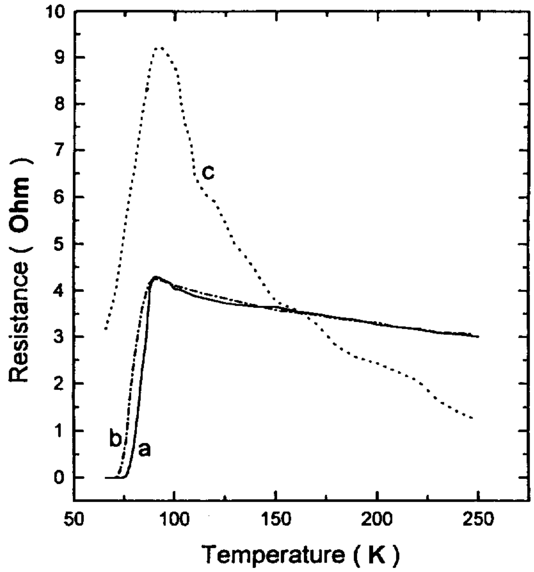

Figure 4. Plot of resistivity of the 1-2-4 as a function of temperature.
a) Na: 10 mg, b) Na: 30 mg, c) Na: 100 mg.

dium substituted compounds of the type $Y_{1-x}Na_xBa_2Cu_4O_{8-y}$, this implies that Na^+ ions can almost completely substitute Y^{3+} within $x=0.16$[11]. Beyond this composition, $BaCuO_2$, Y_2O_3 and CuO phases are formed as a major impurity. Figure 3 displays the X-ray diffraction (XRD) patterns of the compounds. The XRD patterns of the sodium substituted phase are almost identical with that of $YBa_2Cu_4O_8$, where all the major peaks are well corresponded to the bulky $YBa_2Cu_4O_8$. But, as the amount of sodium is increased, superconducting main peak (004) is decreased, impurity peaks, (005), (006) are increased. And $2\theta=47°$, (200), (020) peaks separated in $YBa_2Cu_4O_8$ are merging to one peak as Na concentration increases.

The deposition was performed with a constant electric field of 600 V for 3 min and the distance between the electrodes was 10 mm. In case the current controlled by Na was 10 mA, the powders were deposited very well. But when the current was low, the powders were not deposited, but when the current was very high, the powders were aggregated on the electrode or suspension was boiled. We used silver substrate as negative electrode. In case using Fe or Cu, Fe was converted to Fe_2O_3 and Cu was partially melted during the heat-treatment.

The temperature dependence of the resistivity of the heat-treated samples were shown in Figure 4(a)-(c). In the case of Figure 4(a), $T_{c(onset)}$ was 90 K-$T_{c(onset)}$ was 79 K in reference 7. But, in the case of Figure 4(c), $T_{c(zero)}$ was not obtained. The resistivity curves represent semiconducting behaviors due to the impurity phases near the transition temperature. The electrophoretically deposited thick films did not exhibited cracks after sintering process. The thickness of a deposited coating films were usually in range of 60-80 μm and were observed by scanning electron microscope. The precise thickness depended upon deposition conditions and the nature of the suspension. The chemical reactions at the $YBa_2Cu_4O_8$/Ag interface occurred in the range of 10 μm, but superconductivity was not depressed. The grains containing 100 mg of Na represented the very coarse-grained structure come from the impurity phases such as CuO, $BaCuO_2$, etc.

In summary, an electrophoretic deposition technique was applied for the thick film deposition of $YBa_2Cu_4O_8$($T_{c(onset)}=90$ K, $T_{c(zero)}=75$ K). Sodium was used to role-play electrolyte and to prevent the powder from settling during the deposition. The silver substrate without buffering layer was used, and the best results were obtained from the conditions of 600 V, 10 mA.

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