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EPD Superconductor Film with Submicron YBCO on Ag Alloy

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ABSTRACT The submicron $YBa_2Cu_3O_x$ powder was prepared by the sol-gel method. The particle size is distributed from 0.2 to 1.0 μm, which benefits to eliminate the micro-cracks formed in the $YBa_2Cu_3O_x$ films deposited by electrophoresis. The powder was single phase of $YBa_2Cu_3O_x$ examined by X-ray diffraction. In the sol-gel process the citrate gel was formed from citric acid and nitrate solution of Y_2O_3, $Ba(NO_3)_2$ and CuO. When pH values were adjusted to 6.4 - 6.7, $Ba(NO_3)_2$ could be dissolved in the citrate solution completely. Appropriate evaporative temperature of the sol-gel formation is discussed. Acetone is used as electrophoreticsolution, in which some water and iodine (0.2 g/l) and polyethylene glycol (2 vol.%) are added. The concentrations of $YBa_2Cu_3O_x$ powders is 20 g/l . The thickness of deposited film could be more than 50 μm in 3 minutes of depositing time. The most EPD films could be 90 K zero resistance and the Jc values were over 1000 A/cm2 (0 H, 77 K).
KEYWORDS $YBa_2Cu_3O_x$ film, Sol-gel powder, Electrophoresis

1. Introduction

High Tc oxide superconducting materials can be used in liquid nitrogen. The cheap cryogenic medium makes the materials promise in many fields, especially the tapes (wires) are designable for power transmission, fault current limiter, and for high strong magnets which could be used for magneticlevitation of transportation vehicles, separation of some mines and polluted water, as well as energy storage[1]. BiPbSrCaCuO system is well known developed in making superconducting tape nowadays in the world, but its critical current decreases very fast with the increasing magnetic field, it is the main drawback to be overcome difficultly.

Therefore scientists make efforts to find effective flux pinning centers in $(BiPb)_2Sr_2Ca_2Cu_3O_y$, mean-while $YBa_2Cu_3O_x$ superconductors, because the irreversibility field (Hirr) of which at 77 K is much higher than that of Bi-based super-conductors, are being tried to fabricate wires or tapes, the 2nd-generation superconducting wires or tapes. The method of powder-in-tube (PIT) used for Bi-based

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superconductors is not suitable for YBaCuO superconductor because the melting temperature of YBaCuO is about 50°C higher than the melting point of Ag.

Recently, the trial that produces biaxially oriented YBCO tape conductors using thin film technology has been activated in Japan, the US and Europe. The successful examples include ion beam assisted deposition (IBAD)[1-3]; modified-bias sputter-ing (MBS)[4]; rolling assisted biaxially textured substrate (RABiTS)[5]; The surface-oxidation epitaxy method (SOE)[6,7] and the metal organic chemical vapor deposition (MOCVD) on flexible metal substrates[8]. All the above methods need to have buffers between metallic substrate and YBaCuO film, and need to be operated in vacuum. The thickness of the films normally is less than 200 nanometers.

In contrast the electrophoretic deposition (EPD) can be operated in air and the film thickness deposited is over 50 micrometer. If the substrates and the post heat treatments are improved effectively, it may be a promise method for the preparation of high Jc and long length YBaCuO tapes. In the experiment it was found that when the conventional sintering powder was used, the micro-cracks appeared in the film due to the big particle size(1-40 μm)[9]. The surface of the film would be smooth and less crack with decreasing particle size. Therefore the sol-gel method was used for the preparation of submicron YBaCuO powder.

2. Preparation of $YBa_2Cu_3O_x$ powder by sol-gel method

2-1 The sol-gel process of submicron $YBa_2Cu_3O_x$ powder

The YBaCuO sub-micrometer powder is prepared by sol-gel method. The chemicals Y_2O_3, $Ba(NO_3)_2$ and CuO, which have the metal atoms ratio of Y : Ba : Cu = 1 : 2 : 3, are dissolved in hot nitric acid. Ammonia is used for adjusting the pH to a appropriate value on which $Ba(NO_3)_2$ could dissolve completely. When the solution is added to citric acid, H3Cit (or $C_6H_8O_7$), the mixed solution becomes blue color. After drying at 90°C, the solution is concentrates and dark blue. When the dry gel is put in Muff furnace at 300°C the solvent evaporates, the gel expands, and after a certain time the dry gel will be spontaneous combustion. The product is black grey powder. The powder is pressed to pellets

and sintered at 880°C for 3 hours, and then cooled to 400°C for oxygenation for 10 hours, the pellets become superconductive.

2-2 The effect of pH value on the formation of the Sol-gel

When $Ba(NO_3)_2$ is solved in the citric acid, Ba^{2+} joins with $H2Cit^-$ to form BaH2Cit+, which is not stable. If pH is lower or some solvent evaporate Ba+ will separate out from the solution as $Ba(NO_3)_2$, white deposition. Ammonia, $NH_3 \cdot H_2O$ is used to adjust the pH values. When pH is over 6.5 the white deposition disappears, and the solution become blue transparent solution. In the experiment pH value of 6.4 -6.7 is suitable.

The citrate solution is put in dry box at 90°C, the volume of solution reduces with the drying time and the solution become viscous. After several hours drying the solution become dark blue, some dry gel appears gradually. Because of the low temperature it will take a week if the whole wet gel transfers to dry gel. At lower drying temperature some of ammonia can evaporate, and the pH value of the solution reduces, which causes the white $Ba(NO_3)_2$ to deposit. In order to reduce the transferring time from wet gel to dry gel the drying temperature is increased to accelerate the evaporation of the solvent.

2-3 Composition of the sol-gel product

In the heat treatment at 600°C the powder would eliminate some organic remains and its volume may slightly expand. After grounding the powder was pressed into pellets and sintered at 880°C under oxygen flow. The XRD of the sintered sample is shown in figure 1, in which all diffraction peaks are from $YBa_2Cu_3O_x$ crystal planes and the impurity phases did not present. Therefore the single phase of $YBa_2Cu_3O_x$ can be concluded for the sol-gel powder.

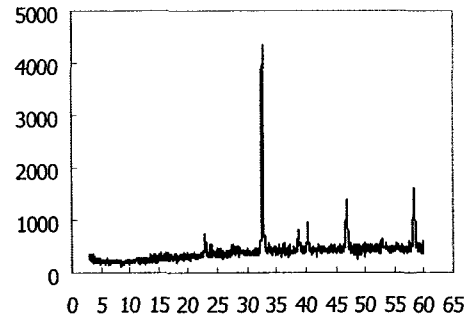


Fig. 1. The X-ray diffraction of YBaCuO powder made by sol-gel and after sintering at 880°C under oxygen flow

2-4 The particle size and the transition temperature of sol-gel $YBa_2Cu_3O_x$

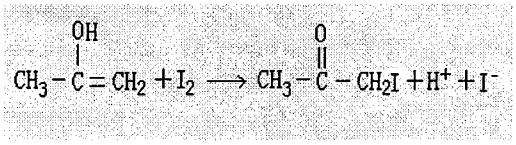
The sol-gel powder was separated by alcohol and particle size was observed by the Scanning Electronic Microscopy (SEM). The particle sizes are in 0.2~1.0 μm. It was found that the ratio of citric acid would affect the particle size, the more citric acid quantity, less particle size of the sol-gel powder.

The sol-gel powder was pressed into 60 mm × 5 mm × 0.5 mm rectangle sample, and the sample was sintered at 900°C for about 5 hours. After sintering the temperature was reduced to 400°C to carry out the oxygenation in oxygen flow for 10 hours. The average transition temperature (Tc) was 91 K, which was measured by standard four line method. Because the size of the sol-gel particle is very small, in the sample the grain boundaries are much more than that in solid sintering ones, which are the obstacles of superconductivities. Therefore the superconducting samples are random in the sintered samples of sol-gel powder. In order to transfer the sol-gel powder to superconducting material, the post heat treatment needs to be studied in detail.

3. Electrophoretic Deposition Using Sol-gel $YBa_2Cu_3O_x$ Powder

3.1 The processing of electrophoretic deposition (EPD)

In the experiment acetone was used as electrophoretic solution, in which some water and iodine were added and following reactions would be happened



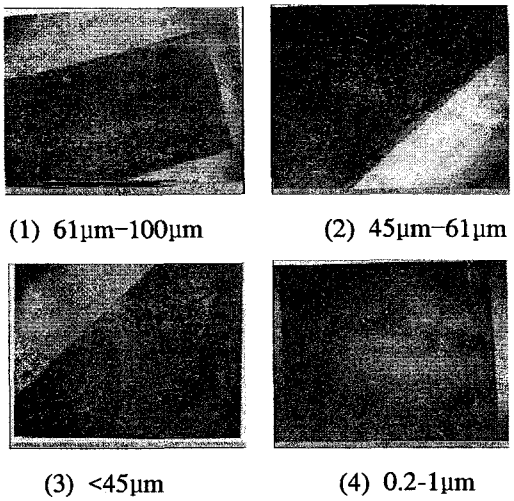
$$CH_3-\overset{OH}{\overset{|}{C}}=CH_2+I_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2I+H^+ +I^-$$

The positive charged hydrogen ions (H+) would be adsorbed on the fine $YBa_2Cu_3O_x$ particles, which would move the cathodes (Ag wire) of the DC electric field and deposited on it. A cylinder shape Ni plate was anode and surrounded the Ag wire. In the solution the concentrations of $YBa_2Cu_3O_x$ powders and iodine were 20 g/l and 0.2 g/l respectively. The distance of cathode and anode was 2 cm. The deposition voltage was 50-120 V, and the solution was stirred in the deposition process by a magnetic stirring device. The thickness of deposited film could be more than 50 μm in 3 minutes depositing time.

3.2 The comparison of the deposited films with different particle sizes

In order to improve the quality of the deposited thick film the effect of $YBa_2Cu_3O_x$ particle sizes were compared. The particle sizes of normal sintered $YBa_2Cu_3O_x$ by powder metallurgy distribute from 1 μm-40 μm, while the thickness of the deposited film is about 40-50 μm only, therefore some cracks occurred in the film. In order to produce flat film surface and to compress the cracks in the experiment the fine YBaCuO powder, diameter less than 1 μm, made by Sol-gel method was used in the electrophoresis solution. In the experiment four samples of YBaCuO powder with different dimensions were used in the solution respectively. The first three samples were selected from YBaCuO powder made by sintering and grinding. Their diameters were (1) 61 μm-100 μm, (2) 45 μm-61 μm and (3) <45 μm respectively. Sample (4) was made by Sol-gel method and the particle dimensions were 0.2- 1.0 μm.

The Four samples were used to deposit YBaCuO films on the Ag plate by electrophoresis under the same electrophoretic parameters.



(1) 61μm-100μm (2) 45μm-61μm

(3) <45μm (4) 0.2-1μm

Fig. 2. Microscopy photos of electrophoresis films deposited from different sizes powders

The morphous pictures from the microscopy observation are shown in figure 2. It can be seen that the surface of sample (1) is very rough and the adherence of the film on the Ag substrate is poor, and after sintering cracks appeared in the film. The surface of electrophoresis deposited film becomes smoother with the decreasing of particle diameters. The surface of sample (4) appears the most smooth and glorious.

3.3 The effect of polyethylene glycol on the $YBa_2Cu_3O_x$ film deposited by EPD

Polyethylene glycol (2 vol. %) was added in the acetone solution as the surface active agent, which could weaken the electrostatic acting force among solid particles, improve

the film surface state and strengthen the adhesion of the film to substrate. Polyethylene glycol could form a plastic layer on the $YBa_2Cu_3O_x$ film and restrain the cracks created in the film. Polyethylene glycol could solve in the acetone completely and after the deposition it could be burn out at about 600°C. The surfaces of EPD films were improved obviously by the polyethylene glycol agent.

3.4 The superconductivity of $YBa_2Cu_3O_x$ deposited by EPD

The sintering of the deposited film was needed to solidify the film and the connection between film and Ag wire. The parameters(speed of increasing temperature; the sintering temperature; the sintering time) in sintering process were important for the film perfection and the superconductivity. If the parameters were not suitable the cracks would occur in the films and the adherence of the film on the substrate was very poor. After the test, the optimum sintering parameters were 2 °C /min. of increasing temperature, 930°C of sintering temperature and 4 hours of sintering time. After sintering, the temperature was reduced to 400℃ to absorb oxygen in pure oxygen for 12 hours.

The transition temperature (Tc) and critical current density (Jc) were measured by standard 4 lines method. The most EPD films could be 90 K zero resistance and the typical Jc values were 1215, 1458 and 1921 A/cm^2 (0 H, 77 K).

4. Conclusions

The submicron and single phase of $YBa_2Cu_3O_x$ powder can be prepared by the sol-gel. All metal nitrates dissolve in citric acid and form the blue solution without white $Ba(NO_3)_2$ deposition when pH value is 6.5. After drying the product is black grey powder. The powder is pressed to pellets and sintered at 880℃ The particle sizes are 0.2-1.0 μm. It is found that the ratio of citric acid would affect the particle size, the more citric acid quantity, the less particle size of the sol-gel powder. The average transition temperature (Tc) is 91 K.

Acetone is used as electrophoretic solution, in which some water and iodine and polyethylene glycol (2 vol.%) are added. The concentrations of $YBa_2Cu_3O_x$ powders and iodine are 20 g/l and 0.2 g/l respectively. The thickness of deposited film could be more than 50 μm in 3

minutes. The most EPD films could be 90 K zero resistance and the typical Jc values were 1215, 1458 and 1921 A/cm^2 (0 H, 77 K).

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