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Preparation of $YBa_2Cu_3O_{7-x}$ superconducting thick films by the electrophoretic deposition method

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Abstract $YBa_2Cu_3O_{7-x}$ thick films have been realised by the Electrophoretic Deposition method (EPD). The influence of several parameters (powder and iodine concentrations in the suspension, applied voltage and deposition time) on the EPD process has been studied by measuring the conductivity of the suspension and the amount of $YBa_2Cu_3O_{7-x}$ particles deposited on the electrode. Superconducting coatings onto silver substrates have been produced by a multilayer process during different deposition times. The highest critical current density value of these coatings measured by the four-point probe method is about 10^3 A/cm^2 (77 K), in a suitable range for magnetic shielding applications.

Introduction

Since the discovery of the superconductivity above the liquid nitrogen temperature, high-T_c superconductivity has been an intensive research field in materials science. Many efforts have been performed to the fabrication of superconducting materials of useful forms. The ceramic character of these materials causes several technological difficulties notably for coatings. Some applications, such as no-loss electrical power transmission, need as high a critical current density (J_c) as possible. Other applications do not necessarily require high values of J_c [1] and low J_c applications have been studied [2, 3]. For magnetic shielding of low frequency magnetic fields, the $YBa_2Cu_3O_{7-x}$ (YBCO) superconductor compound displays very promising properties.

In a practical view, the technique used to realise magnetic shielding devices has to be able to cover large areas of complex shapes presenting uniform properties. Amongst the thick film technologies, the Electrophoretic Deposition (EPD) method meets these requirements. Realisation of a coating by EPD is based on the migration of charged particles between two electrodes [4, 5]. When a voltage is applied, migration of particles in the suspension occurs and finally the film grows on one electrode. After the deposition, a thermal treatment is required to densify the coating. EPD has growing applications to produce coatings, free-standing objects, laminated or graded materials with various materials as Al_2O_3, SiO_2, YSZ... [6].

The feasibility of electrophoretic deposition of YBCO has already been reported. However only a few studies [7–9] have investigated EPD parameters. In the present work we have studied the influence of several parameters: iodine content, initial concentration of YBCO particles, voltage and deposition time. In the second part of this work, we report about the microstructure and the electrical properties of YBCO films deposited by EPD on silver substrates.

Experimental

$YBa_2Cu_3O_{7-x}$ coatings were produced by electrophoretic deposition of a spray-pyrolyzed powder used as purchased from Alfa-Aesar (99.9%, ref. 39534). The

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suspensions were prepared as follows : iodine was first added in 100 ml of technical grade acetone, the YBCO particles were then dispersed in the solvent by ultrasonification during 15 min. The electrophoretical migration of the particles was performed by applying a constant DC voltage (Helwett-Packard 6516A or Apelex PS9009TX power supply) between two electrodes kept to a constant distance of 10 mm.

In the first part of this work, Ni electrodes (Goodfellow, 99%) were used as substrate (40 × 15 × 0.5 mm) and counter-electrode (40 × 30 × 0.5 mm). Several experimental parameters were varied in order to study their influence on the EPD process.

In the second part of this work, YBCO coatings were deposited for characterization of the superconducting properties. Silver substrates (Goodfellow, 99.95%) were used as cathode (0.8 × 4 × 0.25 mm) and a 150 V voltage was applied to acetone suspension containing 1 g/100 ml YBCO and 20 mg/100 ml I_2. For each sample, four successive layers were deposited with intermediate thermal treatment at 920 °C during 1 h in air (100°/h heating and cooling rate). The final heat treatment was performed at about 925 °C during 16 h in Ar atmosphere (60°/h heating and cooling rate). Oxygenation of YBCO phase was finally carried out at about 500 °C during 30 h. The first layer for all samples was realised by electrophoretic deposition during 10 s. The four samples differ by the deposition time of the three following layers: 10, 20, 30 or 60 s for the four different samples.

The mass of YBCO deposited on the electrode (mg/cm^2) was measured using an electronic balance. The conductivity of the suspension was measured with a Metrohm 644 Conductimeter. The coatings were characterized by XRD (Siemens D5000, Cu K_α radiation) and scanning electron microscopy SEM (ESEM Philipps, FEG-XL30). Critical temperature (T_c) measurements were performed with a Physical Property Measurement System from Quantum Design and the critical current density (J_c) by the four-probe technique using the 1 μV/cm criterion at 77 K.

Results and discussion

EPD parameters

The basic equation of EPD kinetics was proposed by Hamaker and Verwey [10]:

$$m = C \cdot u_e \cdot S \cdot E \cdot t \qquad (1)$$

where m is the deposited mass (g), C the suspension concentration (g/cm^3), u_e the electrophoretic mobility (cm^2 s^{-1} V^{-1}), S the deposit area (cm^2), E the electric field in the suspension (V cm^{-1}) and t the deposition time (s). The deposited mass of coatings is related to these different parameters.

In order to study the application domain of Eq. 1 in the case of YBCO suspensions, YBCO deposits have been prepared using different suspension concentrations and EPD parameters. Coatings with homogeneous crack-free surfaces are obtained in all cases except when the voltage exceeded 300 V. The same YBCO powder was used for all experiments (see electron micrograph in Fig. 1). The particle size distribution is comprised between 2 and 6 μm.

In most studies of YBCO electrophoretic deposition [7–9, 11], iodine (I_2) is added to the ketone suspension in order to try to increase the deposit mass. In the following, the influence of iodine is studied for iodine content up to 25 wt% (based on solid content). That value may seem high when compared to typical concentrations of other suspension additives, acting as dispersants or binders, but corresponds to the range usually studied in the YBCO EPD literature [7–9, 11].

Figure 2 presents the influence of the iodine content on the deposit weight per surface unit when a 200 V voltage is applied during 1 min to a 1 g/100 ml YBCO suspension. Particle migration always occurs toward the negative electrode (cathode), revealing a positive charge around the YBCO particles. Addition of iodine appears to lead to a decrease of the deposit weight and it turns out that YBCO deposits can actually be obtained without the presence of iodine in the suspension. However, during previous experiments with YBCO powders prepared by different synthesis, we observed that reproducibility can be poor when no iodine is used. This is probably due to the different surface states of the particles depending on the synthesis

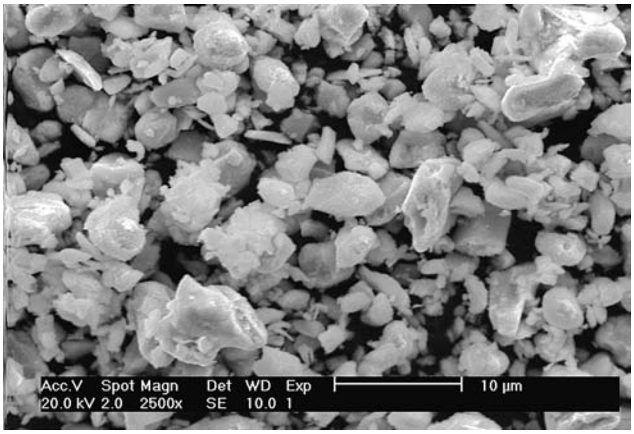

Fig. 1 Electron micrography of the YBCO powder

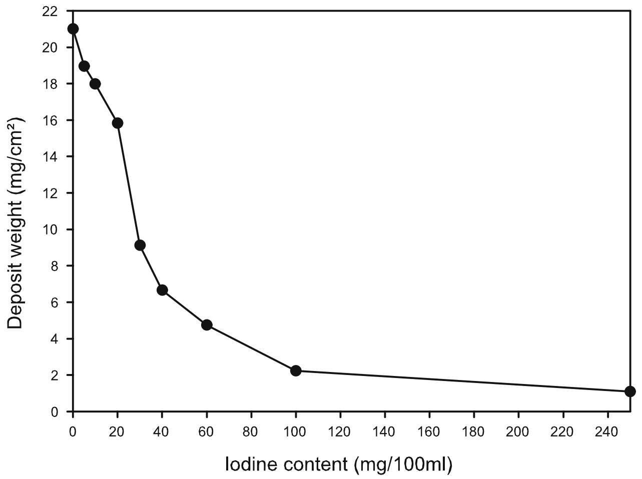

Fig. 2 YBCO deposit weight as a function of the iodine content in the suspension (EPD parameters: 200 V, 1 min, 1 g YBCO/100 ml)

method. Indeed powders synthesised by solid state reaction, coprecipitation or spray-pyrolysed do not show the same deposited weight for the same experimental conditions.

The decrease of the deposit weight resulting from iodine addition was investigated by means of conductivity measurements. Figure 3 shows that iodine addition in acetone increases the suspension conductivity. Without YBCO particles, the conductivity increases linearly with the amount of iodine added in acetone. Addition of 1 g of YBCO powder followed by sonification does not modify that behaviour but the conductivity values decrease by 50%. These results can be qualitatively explained by a mechanism proposed by Koura et al. [8]: charge formation in the suspension is assumed to result from a release of free H^+ due to the reaction of iodine with acetone. Protons are then adsorbed on the YBCO particles leading to positively charged particles. The decrease of conductivity observed when YBCO particles are added to the iodine-acetone mixture would thus result from the decrease of free H^+ ions in the suspension due to adsorption on oxide particles [8, 11]. Increasing the iodine content creates more free protons which participate to the migration and lead to a decrease of the particles deposition on the cathode [12, 13]. Further investigation is under way in order to get more insight into that issue.

As a compromise between reproducibility and deposition rate, a 20 mg/100 ml iodine concentration was chosen for all the following depositions.

Figure 4 shows the influence of the YBCO initial concentration on the deposit weight after applying 200 V during 1 min. When the initial YBCO concentration increases, the amount of particles deposited on the electrode increases but the efficiency {calculated as (deposit weight/ initial weight)*100)} decreases. For initial concentration larger than 0.75 g YBCO/100 ml, the EPD kinetics appears to deviate from the linearity predicted by Eq. 1. Preliminary results of conductivity measurements seem to indicate that the conductivity of the suspension does not increase continuously with the concentration but reaches a maximum and finally decreases for the largest concentrations. This behaviour could be related to the decrease of the I_2/YBCO ratio when initial concentration increases. These issues require additional investigation and will be dealt with in future work.

The influence of the applied voltage on the deposit weight is shown in Fig. 5. The deposit weight increases when the voltage is increased from 100 to 800 V, as

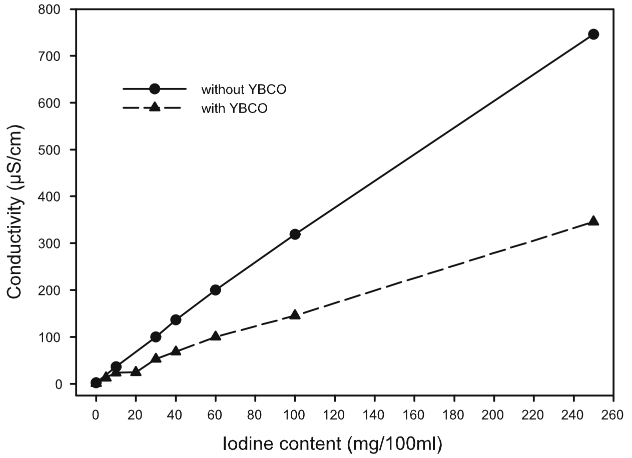

Fig. 3 Conductivity of the suspension as a function of the iodine content

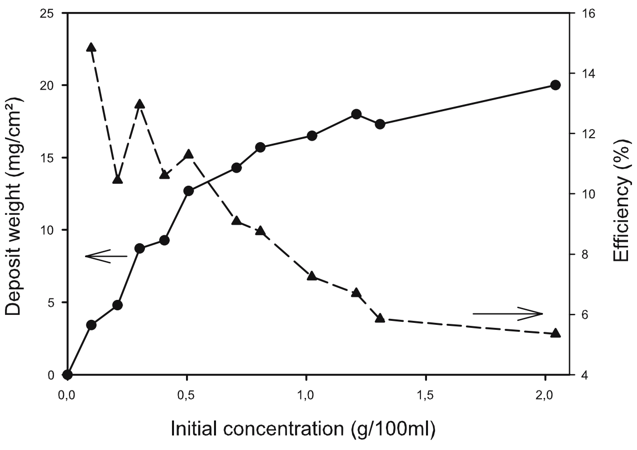

Fig. 4 YBCO deposit weight and efficiency as a function of the initial concentration of YBCO particles in the suspension. (EPD parameters: 200 V, 1 min, 20 mgI_2/100 ml)

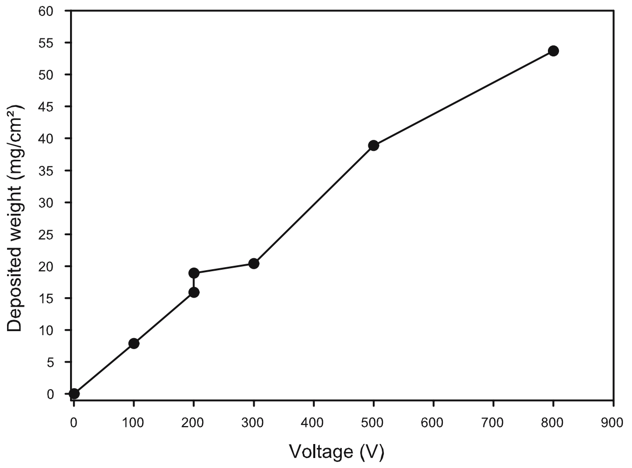

Fig. 5 Deposit weight of YBCO particles as a function of the voltage applied in the suspension (EPD parameters: 1 min, 1 g YBCO/100 ml, 20 mg I_2/100 ml)

predicted by Hamaker equation where the voltage appears through the electric field *E* parameter. However, above 300 V the coating surface is damaged probably due to bubble formation at the electrode surface.

Up to this point, all experiments were carried out with a constant deposition time. However the properties of the suspension are progressively modified during the deposition process. Figure 6 shows the time dependence of the current density during deposition, for different voltages. As expected for constant-voltage EPD [4], the current density decreases during deposition and typically approaches ~0.2 mA/cm^2 after several minutes. As a result, the deposition rate decreases during deposition, as shown in Fig. 7 where the curves of deposit weight (and efficiency) versus time deviate from linearity and reach an approximately constant value after 180 s.

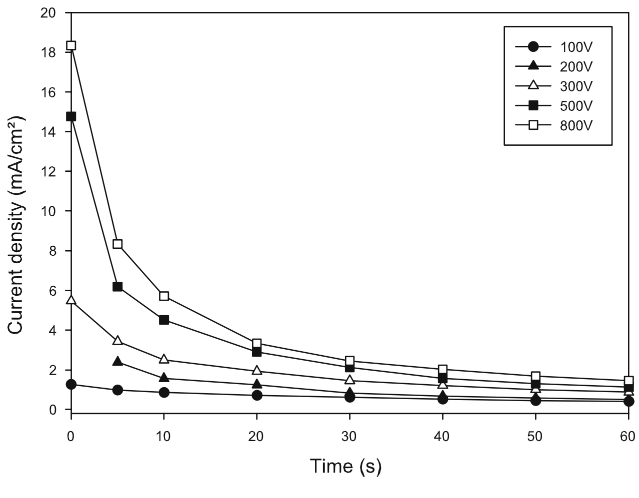

Fig. 6 Current density as a function of time for different voltages (EPD parameters: 1 min, 1 g YBCO/100 ml, 20 mg I_2/100 ml)

The current density *I* in the suspension is related to the electric field *E* and the conductivity σ by the equation:

$$I = \sigma \cdot E \tag{2}$$

The decrease of the current density during deposition can therefore be explained by a decrease of the suspension conductivity and/or by a decrease of the electric field in the suspension: (1) The conductivity of the suspension is expected to decrease during deposition due to the decrease of the concentration of YBCO particles in the suspension. This effect is small at low voltages since the efficiency of the deposition does to exceed about 10% after 1 min (see Fig. 7). (2) Although a constant voltage is applied to the electrophoresis cell, the electric field felt by the suspension will decrease during deposition if the resistivity of the YBCO deposit is larger than the resistivity of the suspension.

Thick films deposition and characterization

$YBa_2Cu_3O_{7-x}$ thick films were prepared on silver substrates in order to characterize their superconducting properties. Considering the results obtained on nickel electrodes in the previous section, the following experimental parameters were chosen: acetone suspension containing 1 g/100 ml YBCO and 20 mg/100 ml iodine, 150 V constant applied voltage. The coatings were prepared by successive depositions of four layers with intermediate thermal treatments (see the experimental section for details). Such a multilayer deposition technique is used in order to deal with stress

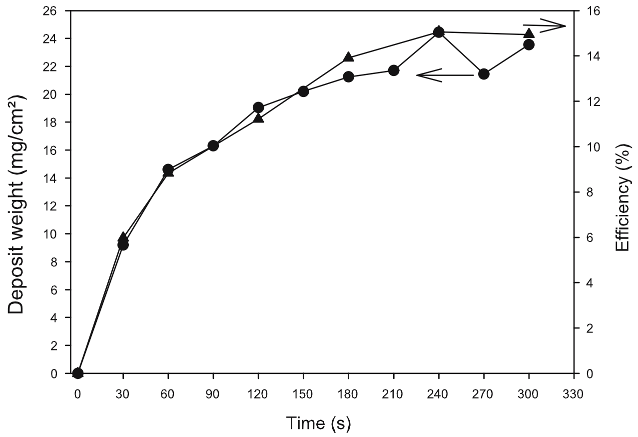

Fig. 7 YBCO deposit weight and efficiency as a function of time (EPD parameters: 200 V, 1 g YBCO/100 ml, 20 mg I_2/100 ml)

problems resulting from the difference between the thermal expansion coefficients of silver and YBCO. Silver was used as cathode because silver is known not to degrade the superconducting properties of YBCO, contrary to other metals and alloys such as nickel or steel.

The films obtained were characterized by X-ray diffraction and the comparison of the diffraction patterns of YBCO powder and coatings shows that no texturation of YBCO films occurs, according to Ondoño-Castillo and Casañ-Pastor [7] for YBCO deposited on tapes. Texturation of YBCO thick films have been already done by EPD using magnetic field during the deposition process [14, 15]. But for magnetic screening applications, isotropy of the superconducting properties is required because electrical devices emit electromagnetic waves in an isotropic way [1]. X-ray diffraction also revealed the presence of secondary phases like Y_2BaCuO_5, as a result of the partial decomposition of YBCO in presence of silver when argon atmosphere is used during heat treatment. Due to the mechanical losses of silver substrates at 930 °C, the maximal heating temperature has to be well below the peritectic temperature of YBCO in air (~1015 °C). Reduced oxygen atmosphere by flowing Ar is so realised to lower the peritectic temperature of $YBa_2Cu_3O_{7-x}$ [16] and improve the connectivity between grains.

The microstructure of the coatings was observed by scanning electron microscopy. Cracks are present in the surface of all samples, especially on thinner films. Polished cross-sections of the different coatings are shown in Fig. 7. Deposition time of individual layers progressively increases from image a to d. (Fig. 8)

Electrical measurements were realised and our coatings lead to a sharp superconducting transition and zero resistivity is reached between 85 and 89 K (T_c). The critical current was also measured. The critical current density J_c values at 77 K are approximatively 630, 325, 630 and 1025 A/cm^2 for the coatings with deposition time of individual layers of 10, 20, 30 and 60 s, respectively. Comparing the J_c values with micrographs in Fig. 7 does not bring out clear correlation. The strong microstructure dependence of the J_c gives difficulties for interpretation on EPD superconductor coatings. Indeed, it is well-established that critical current density depends drastically on the quality of the inter-grain links. Similarly, Bhattacharya et al.[17] concluded to a dimensional dependence of J_c due to microstructural effects. More investigations on this issue have to be pursued. However we can say that the coating with the longest deposition time of individual layers displays a critical current density value above 10^3 A/cm^2 at 77 K, useful for magnetic shielding applications.

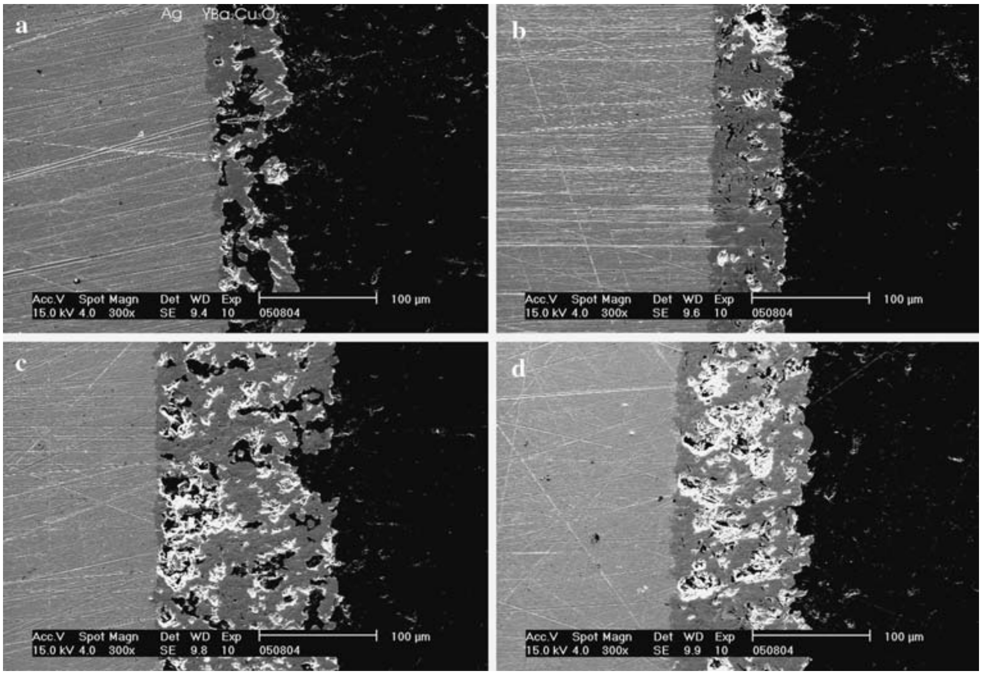

Fig. 8 (**a**) SEM micrography of coating (deposition time of each layer: 10 s) (**b**) SEM micrography of coating (deposition time of each layer: 20 s) (**c**) SEM micrography of coating (deposition time of each layer: 30 s) (**d**) SEM micrography of coating (deposition time of each layer: 60 s)

Conclusions

Superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) coatings have been deposited by the EPD method. The influence of several parameters (YBCO and I_2 concentrations in the suspension, applied voltage and deposition time) on the EPD process has been studied, with reference to Hamaker equation. A set of parameters suitable for YBCO deposition has been found: acetone suspension containing 1 g/100 ml YBCO and 20 mg/100 ml iodine and 150 V constant applied voltage.

Using these parameters, YBCO thick films with different deposition times have been produced on silver substrates and characterized. All films display superconducting properties with a T_c of ~90 K. The highest critical current density J_c obtained is above 10^3 A/cm^2 at 77 K, in a suitable range for magnetic shielding applications.

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