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$YBa_2Cu_3O_{7-\delta}$ thick films on Ag prepared by the Electrophoretic Deposition technique

L Dusoulier[1,2*], S Denis[2,3], J-F Fagnard[3], C Henrist[4], B Vanderheyden[3], Ph Vanderbemden[3], A Rulmont[1], M Dirickx[2], M Ausloos[5], R Cloots[1] and B Vertruyen[1]

[1] SUPRATECS, Chemistry Institute B6, University of Liège, B-4000 Liège, Belgium

[2] SUPRATECS, Communication, Information Systems and Sensors Department; Royal Military Academy, B-1000 Brussels, Belgium

[3] SUPRATECS, Department of Electrical Engineering and Computer Science B28 University of Liège, B-4000 Liège, Belgium

[4] Center for Applied Technology in Microscopy (CATμ), University of Liège

[5] SUPRATECS, Physics Institute B5, University of Liège, B-4000 Liège, Belgium

*E-mail: L.Dusoulier@ulg.ac.be

Abstract. $YBa_2Cu_3O_{7-\delta}$ thick films have been deposited onto Ag substrates by the Electrophoretic Deposition (EPD) technique. Different microstructures and electrical behaviours were observed depending on the starting powder. Coatings prepared from commercial powder displayed significant porosity and the superconducting transition width was found to be magnetic-field dependent. Films produced from home-made coprecipitated powder are denser but contain some secondary phases. No dependence of the resistive transition as a function of magnetic field ($H \leq 20$ Oe) was observed in that case.

I. Introduction

Applications of high-Tc superconductors require the development of an appropriate methodology to produce films with good superconducting properties. In particular magnetic shielding, based on low J_c applications [1,2], needs the development of a process suitable to realize large coatings of complex shape. Electrophoretic Deposition (EPD) is a well-known convenient method to produce thick ceramic films on large area substrates [3,4,5]. The main advantage of EPD compared to other thick film deposition processes is its ability to cover various shapes. The formation of the coating is based on the migration of particles between two electrodes. To obtain $YBa_2Cu_3O_{7-\delta}$ (YBCO) films [6,7,8], particles are first positively charged in acetone medium in presence of I_2. The next step is the application of a voltage between electrodes in the suspension. A migration of particles occurs and finally the film grows on the negative electrode (cathode).

2. Experimental

Two powders with different microstructures were used : a YBCO commercial powder synthesized by spray pyrolysis was purchased from Alfa-Aesar (99.9%, ref. 39534) and a YBCO powder with tabular

grains was prepared by the oxalate coprecipitation method. For so doing, nitrates salts of Y, Ba and Cu were dissolved in water. After complete dissolution, oxalic acid (10%mol in excess) was added to the solution and the pH was adjusted to 7.5 with ammonia. The blue filtered precipitate was heated up to 900°C to obtain YBCO powder. In order to promote the grain growth an additional sintering step at 950°C was performed during 12h.
A suspension containing 10g/l of YBCO powder and 200mg/l of I_2 in 100ml of acetone was treated during 15 minutes in an ultrasonic bath. Ni and Ag tapes were used as anode and cathode respectively. The distance between electrodes was fixed at about 1 cm. 150 V was applied during 3 minutes to produce the coatings. Multilayer coatings were prepared as follows : the first two layers were sintered in air at 920°C during 1h, and the final layer was heated up to 925°C during 12h in Ar atmosphere (the heating and cooling rates were fixed at 100°C/h). The superconducting orthorhombic YBCO phase was recovered by annealing at 520°C during 30h in oxygen flux.
X-ray diffraction analysis was performed with a Siemens D5000 diffractometer (Cu K_α radiation). The coating microstructure was analysed by scanning electron microscopy (Philips FEG-XL30). Secondary phases were put into evidence by back-scattered electron imaging and Energy Dispersive X-Ray (EDX) analysis. Electrical resistance measurements as a function of temperature and magnetic field were carried out with the four-probe technique in a PPMS (Physical Property Measurement System from Quantum Design).

3. Results and discussion

In this study, electrophoresis of particles with various sizes and shapes has been considered in order to increase the bulk density of the deposit and to minimise the number of weak links for electrical currents. The commercial powder (hereafter called « YSP powder ») is made of grains with various shapes and sizes between 2 and 6µm. The home-made powder synthesized by the oxalate coprecipitation method (hereafter called « YOX powder ») is made of big agglomerates (< 30 µm) and small grains with tabular shape.
Figures 1(a) et (b) show the X-ray diffraction patterns for coatings produced from YSP and YOX powders respectively. In the case of the YOX coating, the enhanced intensity of the (00l) reflections suggests that a preferential orientation is reached with a majority of grains having their c-axis perpendicular to the substrate. Indeed, tabular grains migrating under electrical voltage naturally tend to produce a “brick wall” structure [7]. X-ray diffraction pattern of the YBCO coating made from the YOX powder also reveals the presence of a small amount of Y-211 and silver.

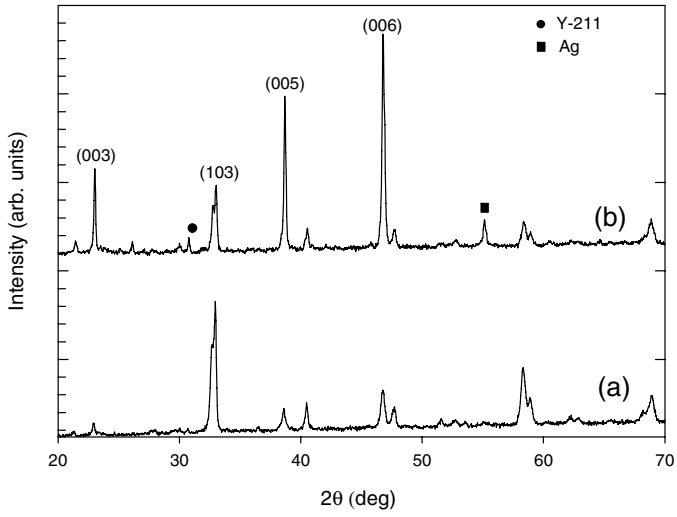

Figure 1. X-ray diffractograms of (a) coating with YSP powder, (b) coating with YOX powder.

The microstructure of the film produced with YSP commercial powder is shown in figure 2 (BSE micrograph). A significant residual porosity is clearly visible and the coating is mainly constituted by Y-123 grains with some silver spots. In figure 3, the coating made from YOX powder, appears much

denser than the YSP deposit. However in the YOX deposit, large amounts of secondary phases were identified by back-scattered electron imaging (BSE) and EDX analysis. CuO phases (dark regions) are present. Y-211 and silver were also detected. These secondary phases probably result from differences in solubilities of oxalate salts during the coprecipitation. Thickness of the two films is about 90 µm and 60 µm for YSP and YOX coatings respectively.

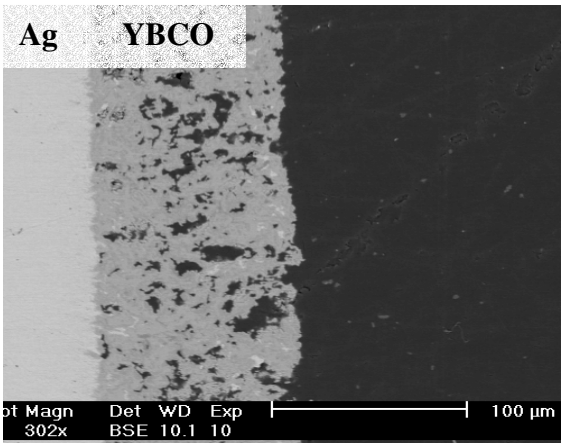

Figure 2. Back-scattered electron micrograph of the coating realised with YSP powder.

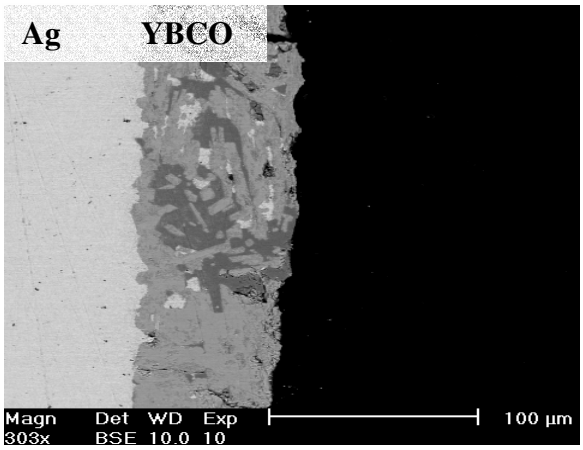

Figure 3. Back-scattered electron micrograph of the coating realised with YOX powder.

Figures 4 and 5 show the temperature dependence of the electrical resistance of the films submitted to different magnetic fields, for the YSP and YOX coatings respectively. The coating realised with the YSP powder has a Tc onset at 90 K with a transition width of ΔT~5 K. By applying a small magnetic field perpendicular to the surface of the coating, the transition becomes progressively broader.

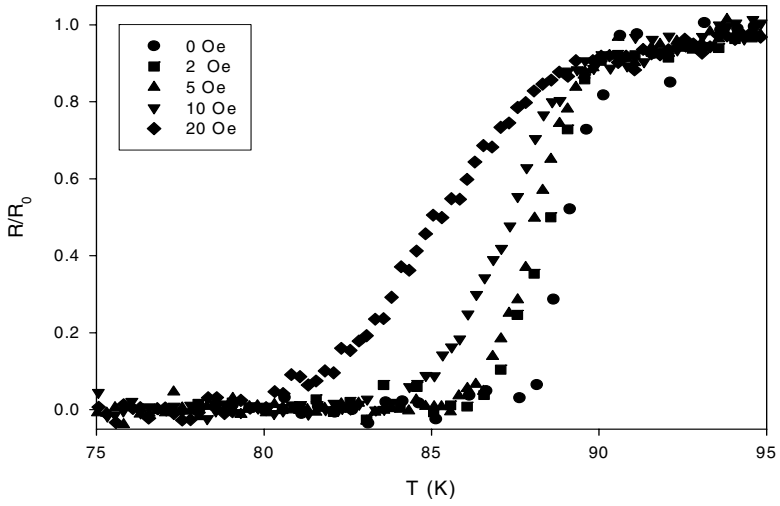

Figure 4. Temperature dependence of normalized resistance in different magnetic fields for YSP coating.

When YOX powder is used to produce the coating (see figure 5), Tc onset is about 90 K with a width of ΔT~5 K, as for YSP coating. However in that case application of a magnetic field up to ~20 Oe does not influence the superconducting transition.

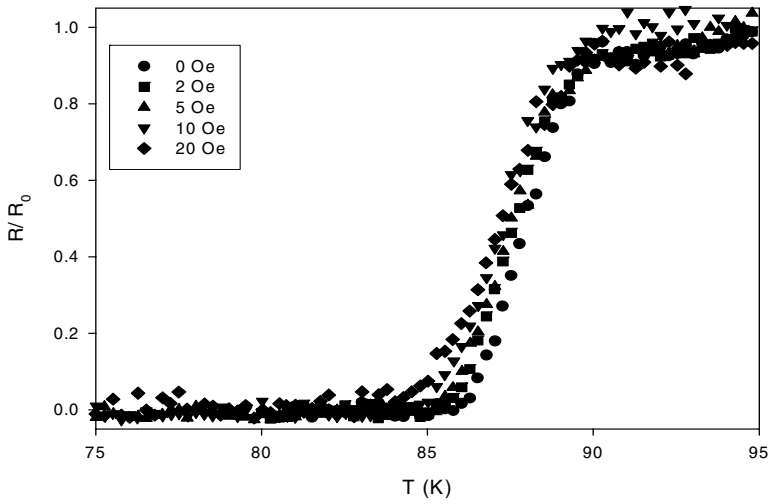

Figure 5. Temperature dependence of normalized resistance in different magnetic fields for YOX coating.

A broadening of the superconducting transition such as observed for the YSP coating can generally be explained by chemical or structural inhomogeneities, which play a dramatic role in determining the intergrain resistivity [9]. The intergrain resistivity is strongly dependent on the intergrain coupling and these junctions can become normal even at low fields. In the case of YSP coating, small particles and poor density could lead to the formation of many weak links resulting in high intergrain resistivity when magnetic field is applied, compared to dense YOX coating constituted by bigger particles. Current versus voltage measurements at 77K (0 Oe) with a 1µV/cm criterion give a current density of about 200 A/cm² and 239 A/cm² for coatings with YSP and YOX respectively. Although the critical current values in zero applied field are similar for the two samples, the YOX coating is a better candidate in view of magnetic shielding application, due to its narrow superconducting transition even in presence of a magnetic field.

4. Conclusions

YBCO coatings have been produced onto Ag substrates by the Electrophoretic Deposition technique. Two YBCO powders with different grain morphologies have been used in order to compare the microstructure and electrical behaviour of the coatings. Commercial powder has led to thick films with a Y-123 stoechiometry but with some residual porosity and a granular structure. Coatings with home-made powder produced by the oxalate coprecipitation method are denser but contain secondary phases, mainly CuO. Electrical measurements have shown interesting features : the superconducting transition is magnetic field independent when the coating has been prepared from the oxalate powder ($H \leq 20$ Oe). Intergrain resistivity appears to have a major influence on electrical measurements in a magnetic field when small particles are used instead of big tabular grains. The influence of the grain shape of starting particles as well as the role of secondary phases are under investigation.

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