

## YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-d</sub> THICK FILMS FOR MAGNETIC SHIELDING: ELECTROPHORETIC DEPOSITION FROM BUTANOL-BASED SUSPENSION

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### Abstract:

Multilayered YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> (YBCO) thick films were coated on silver substrates by electrophoretic deposition (EPD) followed by heat treatment. A butanol-based YBCO suspension is used instead of the common acetone-iodine combination. Tests with several dispersing agents reveal that a branched polyethyleneimine (PEI) dispersant develops large positive surface charge on suspended YBCO particles. As a demonstration of the performance of this new suspension formulation, a 12-layer 100 μm-thick YBCO coating was deposited on an Ag tube. The superconducting transition is sharp with onset critical temperature at 92 K. The sample can shield a magnetic field of ~ 1.3 mT at 77 K, i.e., the best value so far for an YBCO coating on a metallic substrate.

**Keywords:** Ceramics, Electrophoretic deposition, Magnetic shielding, Superconductors, Thick films

### 1. Introduction

Applications of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-d</sub> (YBCO) superconductors involving shielding of low-frequency magnetic fields (< 1 kHz) [1-8], require the fabrication of superconducting screens of various geometries and sizes. Amongst the possible techniques to prepare polycrystalline coatings, ElectroPhoretic Deposition (EPD) appears to be particularly relevant since it enables deposition of YBCO thick films on any metallic substrate, even of complex geometry. Deposition proceeds by applying an electric field to a non-aqueous suspension of charged YBCO particles, using the metallic substrate as one of the electrodes [9,10].

YBCO suspensions are often prepared using acetone as liquid medium and iodine as dispersing agent [11-13]. However, there are some significant drawbacks: (i) the suspension properties depend on the water content in acetone and (ii) the high vapor pressure of acetone at room temperature (due to its 55 °C boiling point) leads to fast drying and frequent macro-cracks. Despite extensive work, we found that we could not further improve the properties of coatings prepared from acetone-based suspensions.

Alcohol-based YBCO suspensions have been occasionally used in the literature as an alternative to ketone-based suspensions [14-17]. Amongst the short-chain (C<sub>1</sub>-C<sub>4</sub>) alcohols, butanol (T<sub>b</sub> = 120°C) has been reported to provide the best suspension stability, probably due to the lowest dielectric constant (ε<sub>r</sub> = 17.1 at 25 °C) [15]. Menhaden fish oil and Emphos PS21A have been used as dispersants for dip-coating [16] and tape casting [17], respectively, but no details were provided in the publications.

In the present work, we have investigated butanol-based YBCO suspensions with four dispersants (I<sub>2</sub>, Menhaden fish oil, Emphos PS21A and branched polyethyleneimine - PEI). The optimized YBCO/butanol/PEI suspension has then been used to prepare a magnetic shield consisting of a superconducting coating deposited on an 8-cm long silver tube.

## 2. Material and Methods

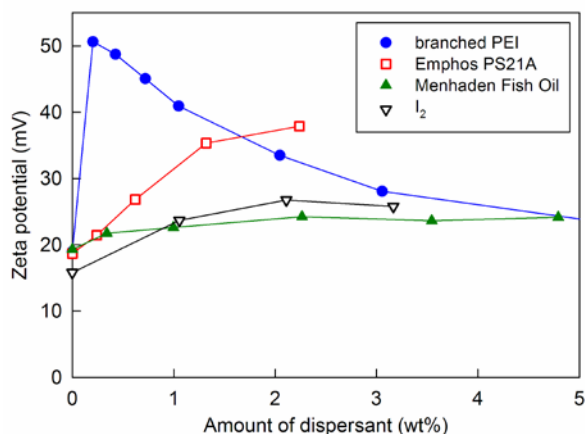
YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  (YBCO) powder was purchased from SCI Engineered Materials (USA) and was milled in acetone for 2 h at 200 rpm in a planetary ball mill (PM 400/2, Retsch) with 1.5 mm zirconia grinding balls. YBCO suspensions (5-10 wt%) were prepared in 1-butanol (99.5 %, Acros Organics) with each of the following dispersants: Emphos PS21A (Witco), Menhaden Fish Oil (Sigma-Aldrich), branched polyethyleneimine (M<sub>w</sub> = 25 000, Sigma-Aldrich) and iodine I<sub>2</sub> (Alfa Aesar). In all cases, the dispersant was dissolved in butanol before addition of the dried milled YBCO powder under stirring. Homogenization of the suspensions was achieved by sonication.

A 10 wt% YBCO suspension in butanol with branched polyethyleneimine dispersant (0.3 wt% with respect to YBCO) was used to coat Ag tubes (99.99 %, Goodfellow). The sample discussed here was prepared by EPD using an Apelex source (PS9009TX) with the following conditions: 50 V potential, 10 mm distance between the Ag cathode and the Ni counter-electrode, 12 layers with 60 s deposition time per layer. After each layer deposition, the sample was removed from the suspension and dried successively at room temperature for 10 minutes and at 70°C for 30 minutes. An intermediate heat treatment at 920°C in air was applied after deposition of the 3<sup>rd</sup>, 6<sup>th</sup> and 9<sup>th</sup> layer to promote adhesion of the coating to the substrate. The final heat treatment was performed at 940°C in argon and followed by a slow cooling (2°C/h) down to 900°C and an oxygenation step for 12 h at 500°C.

Sonication of the suspensions was carried out with an ultrasonic dispersion probe (UP 400S, 24kHz, Hirschler). Zeta potential and particle size were measured using an electroacoustic spectrometer (DT-1200, Dispersion Technology Inc.). Sedimentation tests were performed using a Turbiscan MA2000 (Formulation). The YBCO coatings were characterized by X-ray diffraction (Cu K <sub>$\alpha$</sub>  parallel beam, D8, Bruker) and scanning electron microscopy (XL 30 FEG-ESEM, FEI). Electrical resistivity measurements were carried out in a Physical Property Measurement System (PPMS, Quantum design) with 1 mA excitation current. Magnetic shielding properties were measured at 77 K in a specially designed setup described elsewhere [18].

## 3. Results and discussion

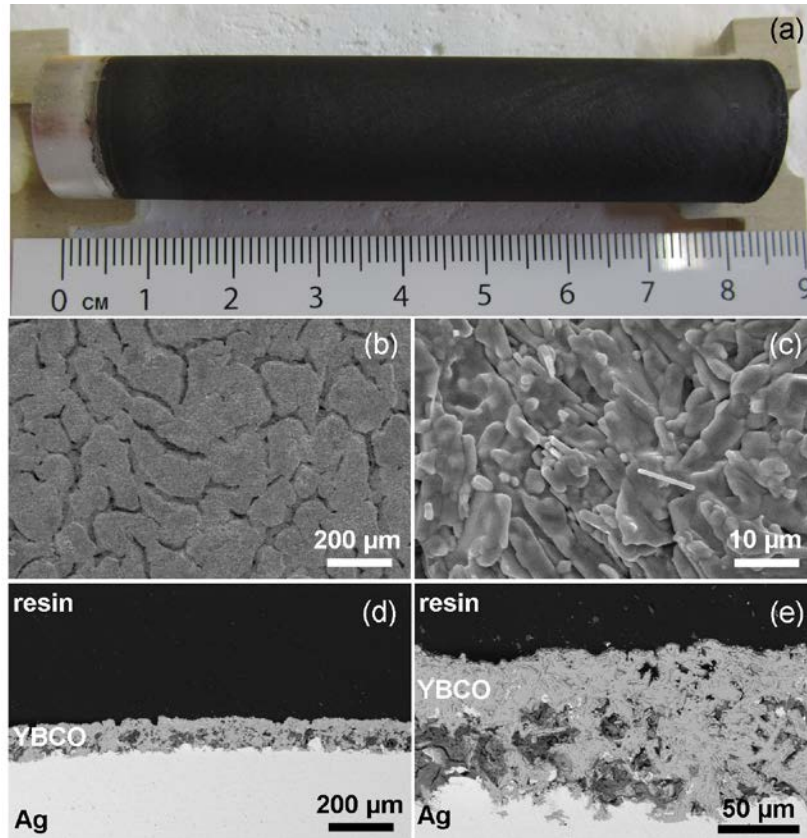
Figure 1 shows zeta potential measurements as a function of dispersant content (in wt% relative to YBCO) for 5 wt% YBCO suspensions in butanol. Menhaden Fish Oil (MFO) is a non-ionic dispersant [19] and does not affect zeta potential significantly. The influence of iodine addition is rather slight in butanol, confirming that the stabilization mechanism in acetone relies on reaction between I<sub>2</sub> and acetone [20]. Both Emphos PS21A (a phosphate ester of ethoxylated hydrocarbon chains [21]) and branched polyethyleneimine (PEI) are found to influence YBCO particles favorably. PEI is especially efficient in creating large positive superficial charge on YBCO particles, probably by protonation of amino groups [22, 23]. Addition of a very small amount (0.3 wt% PEI) results in large values (~ +50 mV) for zeta potential and a decrease in apparent particle size from 0.8  $\mu$ m to 0.4  $\mu$ m. This PEI content corresponds approximately to the adsorption of 1.3 mg of PEI per m<sup>2</sup> of YBCO surface area, in good agreement with the experimental value reported [24] for alumina suspensions.



**Fig. 1.** Zeta Potential as a function of dispersant content (in wt% relative to YBCO) added to 5 wt% YBCO suspensions in butanol. Lines are guides for the eyes.

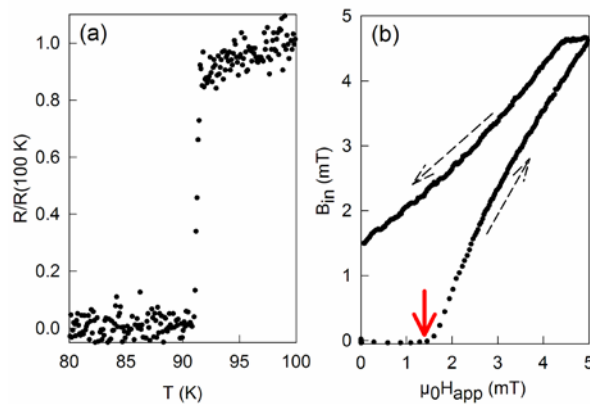
Since zeta potential measurements do not provide information about steric stabilization, the overall stability of YBCO/butanol/PEI and YBCO/butanol/MFO suspensions has been assessed by sedimentation experiments (not shown) using turbidimetry. Sedimentation is considered to start as soon as transmission exceeds 1 % in the top layer of suspension. Using this criterion, we found that MFO does not improve the suspension stability while addition of 0.3 wt% PEI increases the stability time from 1.5 h to 15 h.

Visual inspection of the coatings prepared by EPD from the YBCO/butanol/PEI suspensions suggests that they contain fewer macrocracks than coatings prepared from acetone-based suspensions. In order to substantiate this qualitative observation, the measurement of the magnetic shielding performance is a good test because it depends on the critical current density  $J_c$ , which is very sensitive to possible cracks impeding the supercurrent flow. Accordingly, a 12-layer YBCO coating on an Ag tube (Fig. 2a) was prepared by EPD using a 10 wt% YBCO/butanol/0.3 wt% PEI suspension following the procedure described in Section 2. As shown by electron micrographs in Fig. 2(b-e), the ~130  $\mu\text{m}$  thick YBCO coating exhibits some porosity but good contacts between grains. The good grain connectivity is confirmed by a sharp superconducting transition in the resistance vs. temperature curve (Fig.3a), with an onset critical temperature of 92 K and a transition width < 1 K.



**Fig. 2.** (a) Photograph of the Ag tube coated with 12 layers of YBCO; (b,c) Secondary electron micrographs of the coating surface; (d,e) Back-scattered electron micrographs of a polished cross-section through the coating.

The magnetic shielding properties have been assessed by applying an axial magnetic field  $\mu_0 H_{app}$  and measuring the magnetic induction inside the tube ( $B_{in}$ ) (see [18] for setup details). Fig. 3(b) shows that the tubular sample is able to shield 1.3 mT at 77 K. This represents a significant improvement, not only by comparison with the coatings prepared by EPD from acetone-based suspensions, but also with respect to the best value published so far for an YBCO coating on a metallic tube (0.7 mT for a 180  $\mu\text{m}$ -thick YBCO film deposited by plasma spraying on a stainless steel substrate [6]).



**Fig. 3.** (a) Temperature dependence of normalized resistance for the YBCO coating; (b) Magnetic induction inside the tube as a function of applied magnetic field ( $\mu_0 H_{app}$ ) at 77 K. Dashed arrows indicate the sequence of increasing and decreasing applied magnetic field. The plain arrow indicates the value of the maximum shielded magnetic field.

## Conclusions

A new butanol-based YBCO suspension has been developed for depositing YBCO on Ag substrates by electrophoretic deposition. PEI (0.3 wt% with respect to YBCO) was identified as a suitable dispersant for generating the necessary positive charge on the surface of the YBCO particles in suspension. A 130- $\mu\text{m}$  thick multilayer YBCO coating was successfully deposited on Ag tubular substrate. The coating thus made was able to shield a 1.3 mT magnetic field at 77 K; this indicates that the connectivity of the YBCO grains is good and that the remaining surface macro-cracks do not hinder efficient current flow. In view of the promising results obtained with the novel butanol-based suspension, a systematic optimization of the deposition and heat treatment parameters will be carried out to attempt to further improve the coating performances.

## Acknowledgements

This work relates to Department of the Navy Grant N62909-10-1-7152 issued by Office of Naval Research Global. NDK gratefully acknowledges the financial support received (opportunity grant) from University of Liège, Belgium.

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