Inkjet printing multi-deposited YBCO on CGO/LMO/MgO/Y_2O_3/Al_2O_3/Hastelloy tape for 2G Coated Conductors

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Abstract—We present the preparation of a new architecture of coated conductor by Inkjet printing of low fluoride YBa_2Cu_3O_7-x (YBCO) on top of SuperOx tape: CGO/LMO/IBAD-MgO/Y_2O_3/Al_2O_3/Hastelloy. A 5-layered multi-deposited, 475 nm thick YBCO film was structurally and magnetically characterized. A good texture was achieved using this combination of buffer layers, requiring only a 30 nm thin IBAD-MgO layer. The LF-YBCO CC reaches self-field critical current density values of J_c~15.9 MA/cm^2 (5 K), ~1.23 MA/cm^2 (77 K) corresponding to an I_c(77K)=58.4 A/cm-width. Inkjet printing offers a flexible and cost effective method for YBCO deposition, allowing patterning of structures.

Index Terms—Coated Conductors, Inkjet printing.

I. INTRODUCTION

NOWADAYS, 2G CCs have demonstrated their high utility for generation, transport and storage of energy applications at liquid nitrogen temperatures [1]. Chemical Solution Deposition (CSD) of YBCO is considered the most cost-effective, efficient scalable method to cover the needs of the CC superconducting market. Slot-die coating has been used by D-Nano (Germany) to achieve CCs with record I_c=300 A/cm-width (77 K) in Europe, within the Eurotapes project [2]. Inkjet printing is another technique, which allows the deposition of different oxides through the use of chemical inks [3],[4]. Inkjet deposition of YBCO films from low-fluorine (LF) precursor solutions has been reported [5]. An advantage of Inkjet printing is that it permits patterning structures. Stripes of YBCO for AC-losses reduction have been successfully prepared on both RABiTs (Rolling-Assisted Biaxially Textured Substrates) [6] and ABAD (Alternating Beam Assisted Deposition) [7],[8] CC architectures. The ABAD method enables the use of a polycrystalline substrate, however it must be textured through a thick layer (> 1µm) of YSZ [9]. In the architecture presented in this paper, a 30 nm layer of MgO prepared by ion-beam-assisted deposition (IBAD) is enough to achieve a good texture, comparable to IBAD-YSZ variants.

II. EXPERIMENTAL

A. Sample Fabrication

A new 2G CC architecture was prepared at Oxolutia, based on the CSD multi-deposition by Inkjet printing of YBCO on top of the tape provided by SuperOx: YBa_2Cu_3O_7-x/CGO/LMO/IBAD-MgO/Y_2O_3/Al_2O_3/Hastelloy. SuperOx tape consists of a 60 µm-thick Hastelloy C276 metallic substrate covered by various vacuum-deposited buffer layers which are used to transfer the texture to YBCO and adjust the lattice parameters: a sputtered Al_2O_3 (70 nm), RF-sputtered Y_2O_3 (10 nm), IBAD MgO (30 nm), RF-sputtered LaMnO_3 (LMO) (30 nm) and a PLD Gd:CeO_2 (CGO) (200 nm) layer [10].

The YBCO chemical solution is deposited on top of this substrate by reel-to-reel Inkjet printing multinozzle deposition. In this work, the YBCO layer was prepared using a low-fluorine YBCO solution, thanks to which the quantity of fluoride was decreased 80% compared to the pure TFA-solution, and the processing time was reduced [11]. The LF YBCO solution (0.5 M) is...
obtained by mixing yttrium trifluoroacetate (TFA) with barium 2-ethylhexanoate and copper acetate in a highly boiling point solvent. After the YBCO deposition, the CC tape is subjected to a thermal process consisting of pyrolysis, growth and oxygenation [12]. Thicker YBCO layers can be achieved by multi-deposition.

In this work we present the structural and magnetic characterization of an optimized CC, with a superconducting YBCO film of 475±25 nm thickness achieved by 5-cycles of multi-deposition (sample LF-YBCO). The superconducting performance of this sample is compared with that of a previously characterized CC also prepared by Inkjet printing, but starting from a 0.5M TFA solution and with a different architecture: TFA-YBa2Cu3O7-x/CZO/ABAD-YSZ/SS [4]. This t=0.9 μm thickness film was obtained after the growth of three cycles of deposition-pyrolysis, and is denoted as TFA-YBCO.

B. Experimental details

The YBCO deposition has been performed using an in-house built inkjet printer using a Konica Minolta piezoelectric printhead with 512 nozzles. The structural characterization by X-ray diffraction was done using a General Area Detector Diffraction System (GADDS) from Bruker AXS, Inc., equipped with a two-dimensional (2D) detector.

The homogeneity of the films after pyrolysis was checked using a Leica DM 1750 M optical microscope. Atomic Force Microscopy (AFM) was used to provide high resolution, 3D information about the surface of the films through the available Agilent 5100 device.

Scanning Electron Microscopy (SEM) of the surfaces was carried out with a high resolution FEI Quanta 200 FEG system. Scanning Transmission Electron Microscopy (STEM) characterization was done using the probe corrected FEI Titan at 300kV and FEI Tecnai Osiris microscopes. High and Low angle Annular Dark Field (HAADF and LAADF) STEM together with Bright Field TEM (BFTEM) imaging and STEM Energy Dispersive X-ray Spectroscopy (EDX) mapping were performed.

The superconducting properties were characterized by DC magnetometry, using a Superconducting Quantum Interference Device magnetometer (SQUID) provided with a 9 T superconducting coil. The magnetic moment of the samples was obtained after subtracting the magnetic contribution from the metallic substrate [13]. AC susceptibility measurements were performed with a Quantum Design Physical Property Measurement System (PPMS) by using amplitudes between μ₀Hac=0.01–1.5 mT and dc-fields in the range of 0–9 T, at frequencies f=1111 Hz.

III. STRUCTURAL CHARACTERIZATION

A. Characterization of the CGO buffer layer

The surface of the CGO cap layer observed by optical microscopy was very homogeneous. The surface topography was further characterized by AFM. Fig. 1(a) shows a topographic image, from which the CGO roughness was determined (rms = 1.7 nm). Following the methodology developed by Coll et al. [14], the percentage of the flat grains (planarity) from this cap layer was found to be 68% (Fig. 1(b)). The topographic image shows the presence of some outgrowths owing to the Pulsed Laser Deposition (PLD) process, whose height does not exceed 20-40 nm.

The structural characterization of the SuperOx tape was performed with a GADDS two dimensional detector (Fig. 2a). The two observed rings correspond to the polycrystalline, Hastelloy C276 metallic substrate, whereas the epitaxial spots correspond to the CGO(200), LMO(001)(002), MgO(200) and Y₂O₃(111) reflections. The width of the ω-scan of the CGO(111) reflection was FWHM=7.4º, while that of the ϕ-scan at the CGO(200) reflection was 2.3º, indicating a good texturing of the CGO cap, better out-of-plane than in-plane.

B. Characterization of the CC tape

The structural and morphological properties of the LF-YBCO sample were investigated combining XRD, SEM and TEM. The microstructure of the YBCO film, crystallized at 790ºC under 200 ppm oxygen partial pressure on top of the SuperOx tape is shown in the SEM micrograph in Fig. 3. The YBCO film shows crack-free microstructure with c-axis oriented grains. Some pores and precipitates rich in copper can be appreciated on the surface.

The XRD pattern of the LF-YBCO sample is shown in Fig. 2(b). A good c-axis orientation of the YBCO layer is demonstrated by the strong intensity of the (00l) spots. The width of the ϕ-scan of the YBCO(103) reflexion was FWHM=3.9º, while that of the ω-scan at the YBCO(005) reflexion was 1.5º, indicating a very good out-of-plane texture, better than in-plane. The improvement in the YBCO texture, sharper than for the CGO (ϕ-scan 7.4º, ω–scan 2.3º) could be a consequence of the epitaxial YBCO, nucleating preferentially on the grains of the cap layer having a lower misorientation and of the lamellar growth of these nuclei to the grain size much larger than that of the CGO.

STEM was used to characterize in more detail the microstructure of the LF-YBCO sample. Fig. 4 shows a low-resolution, cross-section image where the different layers of the CC architecture can be identified. Note that there is a reacted phase present at the interface between the cap CGO and the YBCO layers, identified as BaCeO3 (BCO).

Further information on the composition of the set of buffer layers was obtained by EDX mapping. Fig. 5 shows the elemental concentration EDX maps obtained for Y, Cu, Ce, Ni, Al, Mg, La (Fig. 5(a)), together with the Ba and Ce maps (Fig. 5(b-c)), measured to elucidate the composition of the reactive phase between YBCO and CGO. From the compositional analysis, the set of buffer layers was confirmed to be Y₂O₃/MgO/LMO. On the surface of the metallic substrate, a passivation layer of about 40-50 nm, formed by Cr and Al, is observed. The major part of the initial 200 nm CGO remains unreacted but a reactive phase (BCO) of about 30-40 nm thick can also be identified in Fig. 5(b-c).
A detail of this reactive layer BCO layer sandwiched in between the CGO and YBCO layers is shown in the TEM image of Fig. 6(a). YBCO grows c-axis oriented on top of BCO, and thus the presence of this partial reactivity does not degrade the superconducting properties.

A deeper characterization of the morphology of the sample was done using HAADF-STEM imaging. The approximate thickness of the YBCO grains observed from various images was found to be ~0.5-1 µm. A high resolution image of the YBCO matrix is shown in Fig. 6(b). The orange arrows indicate high number of short Y2BaCu6O16(Y248) intergrowths. Some triple Cu chains are incorporated in these Y248 phases, resulting in local Y125 intergrowths.

IV. MAGNETIC CHARACTERIZATION

The magnetic hysteresis loops measured for the LF-YBCO sample for a maximum applied field of \( \mu_0H_{max}=5 \) T at 5, 50 and 77 K after subtracting the substrate contribution is shown in Fig 7(a). The \( M(H) \) cycles exhibit a maximum on the reverse branch of the magnetization at positive applied magnetic fields (Fig. 7(a), inset), a feature associated to granularity [15], vide infra. The percolating, inter-grain critical current density field-dependence is determined from these saturated loops applying Bean’s approximation for a thin disc, \( J_{cGB}(H)=3M(H)/R \), where \( R \) is the effective radius of the sample (Fig. 7(b)). The LF-YBCO reaches self-field critical current density values of \( J_{cGB}\approx 15.9 \) MA/cm\(^2\) (5 K), ~6.06 MA/cm\(^2\) (50 K) and ~1.23 MA/cm\(^2\) (77 K). This corresponds to a current per centimeter width of \( I_c=58.4 \) A/cm-width.

For the sake of comparison, the percolating critical current at the same temperatures of the previously reported ABAD CC sample is also shown in Fig. 7(b). The values of \( J_{cGB} \) reached in self-field by the LF-YBCO sample are slightly above those of TFA-YBCO. The intergranular \( J_{cGB}(H) \) dependence of the two samples is qualitatively similar to that reported for other CCs [13]. It is observed that while the plateau at low fields and crossover to the \( J_{cGB}=H^{0.5} \) region is similar for the two samples, the decrease of \( J_{cGB}(H) \) occurs at smaller fields for the LF-YBCO, reflecting a somewhat smaller irreversibility line. This might be related to the presence of a large density of short stacking faults observed by STEM in Fig. 6(b), which have been reported to break the length of twin boundaries, decreasing the vortex pinning efficiency at high fields [16].

In order to further characterize the granularity of the LF-YBCO sample, we applied the method developed by A. Palau et al. [15] to simultaneously determine the grain size \( <2a> \), intergranular \( J_{cGB} \) and intragranular \( J_{cG} \) critical currents from the measurement of \( M(H) \) minor loops, showing a progressive saturation of the granularity peak (Fig. 8a).

From the experimentally determined values for the saturation field of the peak, \( \mu_0H_{peak}^{sat}=422 \) mT, and the maximum field at which the remanent magnetization saturates, \( \mu_0H_{m}(M_{rem}^{sat})=292 \) mT (Fig. 8b), we estimated a grain diameter of \( <2a>\approx 0.80\pm0.05 \) µm, compatible with the grain size found by TEM (~0.5-1 µm) [17]. Furthermore, the intragrain critical current density determined was \( J_{cG}(5K)=49\pm2 \) MA/cm\(^2\) and the inter-to-intragrain critical current density ratio is \( J_{cGB}/J_{cG}=0.3 \). Comparing the granular characteristics of the LF-YBCO tape and previously reported TFA-YBCO tape (Table 1), the following conclusions can be drawn. First, it is observed that the deposition of YBCO on the SuperOx tape results in a smaller size of the grains, something not surprising since the two utilized substrates are different. Besides, a high \( J_{cG} \) is attained for LF-YBCO sample, even larger than that of TFA_YBCO. However, the inter-to-intragrain critical current density ratio determined at 5 K is smaller for the LF-YBCO \( (J_{cGB}/J_{cG}=0.32) \) than for the TFA-YBCO \( (J_{cGB}/J_{cG}=0.46) \). The diminished intergranular performance may be due to different degrees of optimized texture qualities in both films [18].

AC measurements were performed in order to investigate the CC homogeneity. Fig. 9 shows the measured temperature dependence of the real and imaginary components of the ac susceptibility, \( \chi ', \chi ''(T) \) in self-field at different ac fields at constant frequency. The critical temperature, measured from the transition of the \( \chi ''(T) \) curve to zero at \( \mu_0H_{c0}=0.1 \) mT was \( T_c=88.5 \) K, with a narrow transition width, defined as \( \Delta T=T_c-T\) (at 0.95\( \chi ''/\chi '0 \)) of \( \Delta T=2.3 \) K. \( T_c \) is slightly smaller than values typically found in thin-films and CCs grown by the TFA CSD method, something which may be explained by the previous mentioned presence of C in the GBs. Fig. 9 shows that the \( \chi ''(T) \) curves measured for the LF-YBCO sample presents a single peak, similar to a non-granular film, i.e., flux penetrates from the surface to the centre of the sample through the homogeneous network of low angle GBs following the critical state [19].

The temperature dependence of the intergranular critical current density was determined from the peaks of the \( \chi ''(T) \) curves measured at different AC field amplitudes, according to: \( J_{cGB}(T_{peak})=2\mu_0H_{c}/1.94t \). The AC determined \( J_{cGB}(T) \) curve corresponding to the main, homogeneous network of low-angle GBs has been extrapolated to the DC data obtained at 5, 50, 77 K, considering that SQUID measurements are only sensitive to the highest \( J_c \) percolative domain. As shown in Fig. 10, the temperature dependence of the percolative critical current is very similar to that earlier found for the TFA-YBCO sample.

V. CONCLUSIONS

We have fabricated a new CC architecture YBa2Cu3O7/CGO/LMO/MgO/Y2O3/Al2O3/Hastelloy based on the low-fluorine chemical-solution route using reel-to-reel Inkjet printing deposition. The total thickness of the YBCO film was 475±25 nm after a 5-multi-deposition process. A good texture of the resulting film was achieved utilizing a very thin 30 nm IBAD-MgO layer. A magnetically homogeneous YBCO films was obtained, exhibiting a self-field percolative critical current density of \( J_{cGB}\approx 1.23 \) MA/cm\(^2\) at 77 K (i.e. an \( I_c=58.4 \) A/cm-width). Scaling of this architecture to 10 m long tapes at Oxolutia is foreseen in the close future.
References


Fig. 1 (a) topographic 1 µm x 1 µm 3D-AFM images of the CGO top layer from the SuperOx tape; (b) binarization of the topographic image, where the flat cerium grains are shown in red.

Fig. 2 2D XRD pattern of (a) SuperOx tape; (a) the LF-YBCO sample.

Fig. 3 High resolution SEM micrograph of the LF-YBCO sample.

Fig. 4 Cross-sectional TEM image showing the CC architecture.
Fig. 5 EDX maps of the whole architecture (a); maps for Ba (b) and Ce (c).

Fig. 6 (a) TEM image of the interface of BCO with YBCO; (b) high resolution HAADF-STEM Z-contrast image showing the stacking defects.

Fig. 7 a) Hysteresis loops for the LF-YBCO sample at T=5, 50 and 77 K. Inset: granularity peaks in the reverse branch of the magnetization; b) $J_c^{GB}(H)$ of the same sample and TFA-YBCO CC [4] for comparison.
Fig. 8 (a) Magnetic hysteresis loops at 5 K measured for the LF-YBCO sample for increasing \( \mu_0 H \) from 0 - 0.8 T; (b) Evolution of the remanent magnetization and (inset) of the peak position \( H_{\text{peak}} \) as a function of the maximum applied field \( H_{\text{m}} \) at 5 K.

Fig. 9 (a) \( \chi'/\chi_0(\text{T}) \) and \( \chi''/\chi_0(\text{T}) \), measured in self-field, at \( f=1111 \) Hz and different AC fields \( \mu_0 H_{\text{ac}} \) for LF-YBCO. Top (inset): zoom of \( \chi''/\chi_0(\text{T}) \) showing the absence of residual peaks.

Fig. 10 Temperature dependence of the intergranular critical current density \( J_{\text{GB}} \) determined from the \( T_{\text{peak}} \) position of the \( \chi'' \) peaks and from SQUID measurements for LF-YBCO and TFA-YBCO sample [4].
<table>
<thead>
<tr>
<th>Parameter</th>
<th>LF-YBCO (0.475 µm)</th>
<th>TFA-YBCO (0.9 µm)</th>
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<tbody>
<tr>
<td>$\mu H_{\text{peak}}$ (mT)</td>
<td>42.2</td>
<td>68.4</td>
</tr>
<tr>
<td>$\mu H_{s}$ ($M_{\text{sat}}$) (mT)</td>
<td>292</td>
<td>360</td>
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<tr>
<td>$\langle \Delta \phi \rangle$ (µm)</td>
<td>0.8±0.5</td>
<td>2.2±0.5</td>
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<td>$J_{c}^{(1)}$ (MA/cm²)</td>
<td>49±5</td>
<td>27±5</td>
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<td>$J_{c}^{(2)}$ (MA/cm²)</td>
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<td>1.23</td>
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<tr>
<td>$J_{c}^{(3)}$ (MA/cm²)</td>
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<td>12.5</td>
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