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Superconducting properties of YBCO coated conductors produced by inkjet printing

Abstract. *Current methods of producing $YBa_2Cu_3O_{7-\delta}$ coated conductors (YBCO CC) require expensive processing. A new technology combining chemical solution deposition (TFA-MOD) with inkjet printing, demonstrated successfully in this paper as confirmed by Hall probe magnetometry, shows considerable potential as a cost-effective replacement. The flexible control of ink stoichiometry and rheology, and the ease of introducing additions, offered by CSD inkjet printing has the potential to reduce the strong I_c anisotropy of YBCO CCs revealed by goniometric I_c measurements.*

Streszczenie. *Nowa technologia produkcji nadprzewodzących taśm $YBa_2Cu_3O_{7-\delta}$, łącząca procedurę chemicznej depozycji roztworu za pomocą drukowania, ma szansę zastąpić obecne, kosztowne metody produkcji. Pomiar magnetometryczny czujnikiem Halla potwierdził nadprzewodnictwo próbki YBCO otrzymanej wyżej wymienioną metodą, która umożliwia łatwą kontrolę stechiometrii i reologii roztworu, a także wprowadzanie dodatkowych komponentów, mających na celu redukcję silnej anizotropii I_c w filmach YBCO, ukazanej przez pomiar goniometryczny. (**Nadprzewodzące właściwości taśm YBCO otrzymanych metodą drukowania roztworu**).*

Keywords: YBCO, sol-gel, Hall probe measurement, goniometric measurement.
Słowa kluczowe: YBCO, sol-gel, pomiar czujnikiem Halla, pomiar goniometryczny.

Introduction

The current methods of producing $YBa_2Cu_3O_{7-\delta}$ coated conductors (YBCO CC) require expensive equipment and often vacuum conditions. An especially promising new chemical solution deposition (CSD) technology combining sol-gel synthesis, based on the trifluoroacetate metalorganic deposition (TFA-MOD) route, with inkjet printing, presents clear opportunities for industrial application. The method enables the controllable deposition of liquid sol on the metallic substrate and does not require expensive equipment and vacuum conditions, significantly decreasing manufacturing costs [1]. Because of the anisotropic properties of superconducting YBCO, the dependence of its superconducting properties on oxygen content, and the weak grain boundaries which impede critical current transport, the deposition and subsequent heat treatment of the YBCO ink must be optimised to obtain a crystallographically well textured and superconducting film. After optimising processing parameters, the YBCO CC obtained from this TFA-MOD route was confirmed to be superconducting by scanning Hall probe magnetometry. Goniometric critical current measurements performed on commercially available YBCO CC indicate a new direction of research towards controlling the anisotropy of this superconductor, as the sol-gel method enables flexible control of the ink stoichiometry and rheology.

Experimental

The YBCO precursor ink was prepared using the trifluoroacetate (TFA) route, from $YBa_2Cu_3O_{6.9}$ powder (SSC Inc.) previously desiccated in a vacuum furnace at 150 °C for 24 h. Anhydrous acetone was mixed with the YBCO powder in the ratio of 15 cm^3 to 3 g. Trifluoroacetic acid (TFAH) was added drop-wise under stirring at room temperature in 10 vol. % excess to the stoichiometric molar ratio of 13:1 (Reaction 1) to ensure full reaction of the YBCO powder. The reaction was run for 24 h at 85 ºC in an N_2 atmosphere. The resulting blue solution was cooled to room temperature and a stoichiometric amount of trifluoroacetate anhydride (TFAA), according to reaction (2), was added drop-wise. The solution was kept for approximately 1 h at 85 ºC (until it became clear and green). Subsequently the resulting green solution was mixed with anhydrous methanol and heated under vacuum in a rotary evaporator three times in turn, at a temperature ranging between 65 and 80 ºC. This product was diluted to the appropriate concentration with anhydrous methanol, resulting in a clear green solution, passed through a 1 μm glass microfibre filter and sealed in a vial under a nitrogen atmosphere. Stored in this way, the ink remained stable and suitable for printing for several months.

(1) $$YBa_2Cu_3O_{7-\delta} + 13\ TFAH \rightarrow Y(TFA)_3 + 2\ Ba(TFA)_2 + 3\ Cu(TFA)_2 + 6.5\ H_2O$$

(2) $$6.5\ H_2O + 6.5\ TFAA \rightarrow 13\ TFAH$$

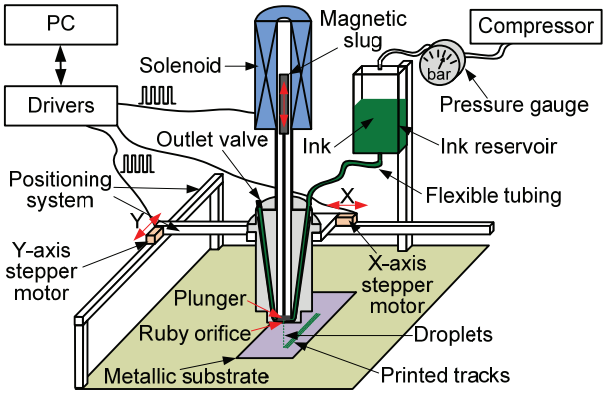

Fig.1. Schematic of the drop on demand inkjet printing system with electromagnetic nozzle. To print continuous tracks, the drivers are set to deliver pulses of current at a rate synchronised with the positioning system velocity.

The prepared ink was deposited on a Ni-5%W rolling-assisted biaxially textured substrate (RABiTS) with a double $La_2Zr_2O_7$ (LZO) buffer layer and a single CeO_2 cap layer (Ni-5%W/2LZO/CeO_2) provided by Zenergy Power GmbH (Germany). The buffered tape was cleaned with ethanol for 3 min and additionally with isopropanol or acetone for 3 min in an ultrasonic bath before each deposition, and used as soon as possible to prevent degradation of the wettability. The ink was deposited on the substrate by means of drop on demand printing using an electromagnetic nozzle (a solenoid micro-valve modified from a Domino MacroJet printer) and other equipment schematically presented in Figure 1. After outgassing, the YBCO ink was supplied to the nozzle from a reservoir under

a constant pressure of 0.15-0.20 bar (relative to atmospheric pressure) generated by a compressor. Typically, the electromagnetic valve was held open for 500 μs. Square patterns were created with appropriate droplet spacing. The printing parameters were adjusted to give complete and uniform coverage of the buffered substrate. The printing procedure was carried out in an inert atmosphere of pure N_2 at room temperature fluctuating between 18 and 25 ºC, with a relative humidity below 20%.

Heat treatment of the samples was performed in a Carbolite horizontal tube furnace with a purpose built valve controller. Pyrolysis was conducted in a wet O_2 atmosphere at 340 ºC; YBCO growth was in wet 200 ppm O_2 in an Ar atmosphere at 730 ºC; oxidation was in a dry O_2 atmosphere at 450 ºC (Fig. 2). The flow rate was always 1.5 L/min. The temperature of the sample was measured by a thermocouple (type K) placed in its vicinity and controlled by a Eurotherm PID controller. A Sensirion humidity sensor was used to measure the humidity of the gas entering the furnace. The heating rate, dwell time and temperature were adjustable under computer control, and were tuned to the process. The three-step heating process is schematically presented in Figure 2.

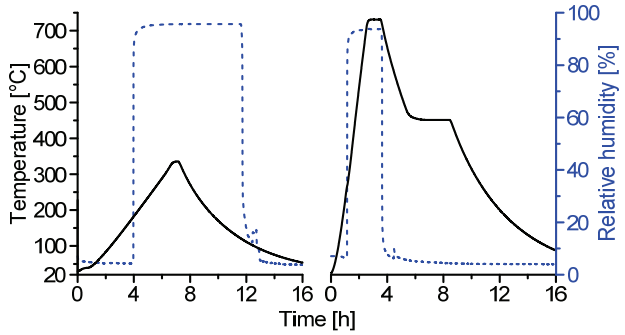

Fig. 2. Heat treatment of the YBCO precursor layer. The heating rates were 1 °C/min and 5 °C/min for pyrolysis and the subsequent YBCO crystal growth respectively. The cooling rate was defined by the heat capacity of the furnace.

The resulting YBCO films were zero field cooled to 77 K and magnetized with a field of 0.1 T applied perpendicular to the tape surface, and subsequently measured using a scanning Hall Probe system as demonstrated by Łekawa et al. [2] to map the trapped magnetic field. The Hall probe active area was 0.1 × 0.1 mm, at a scan height of 0.2 mm and with a step size of 0.2 mm. The trapped field profile indicates the regions with critical current density, J_c, above 0.2 MA/cm^2.

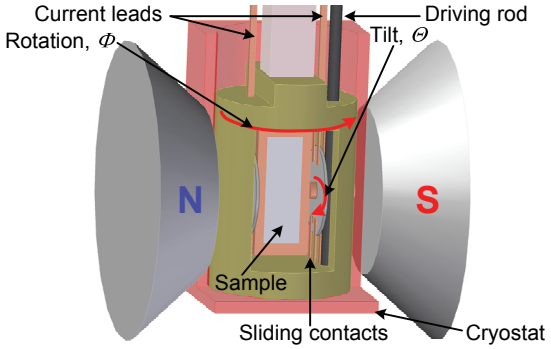

Fig. 3. Experimental set-up of the two-axis high current goniometer.

A high transport critical current measurement system has been developed based on a two-axis goniometer probe (Fig. 3). The probe is supported vertically between the poles of a fixed electromagnet, and the sample can be precisely oriented around two perpendicular axes using computer-controlled stepper motors. The whole probe can rotate about its long axis (*Rotation, Φ*), and a moving sample platform can rotate about a perpendicular axis through the mid-point of the sample platform (*Tilt, Θ*) [3,4].

Tape samples 36 mm long were mounted on a rotating platform, with the length of the tape parallel to the current and a voltage contact separation of 6 mm. Measurements were performed in liquid nitrogen with an applied field of 0.6 T. The critical current was measured as a function of two-axis orientation, extracting critical current, I_c, and the n-value from automated power-law fits with a 1 μV/cm electric field criterion.

Results

An optimised processing procedure resulted in YBCO with 5.14° out-of-plane (XRD Cu-Kα θ-scan (005) at Ω = 19.26°) and 7.76° in-plane grain misalignment (Φ-scan (103) at 2θ = 32.84°) and acceptable morphology as indicated by the pole figure scan ((103) at 2θ = 32.84°) and scanning electron microphotograph, all presented in Figure 4.

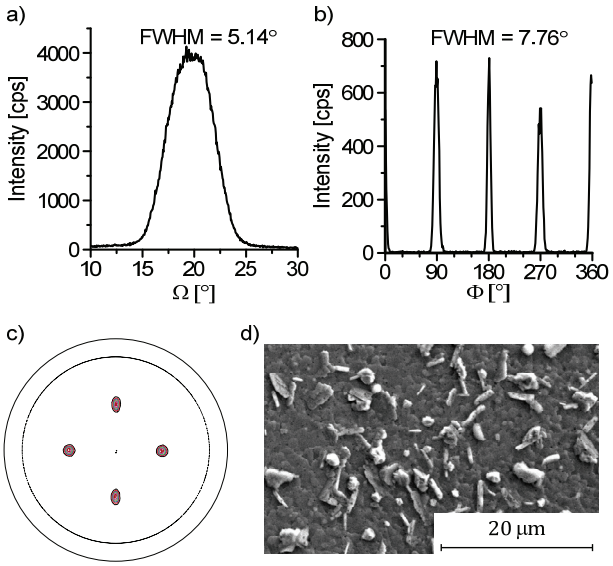

Fig. 4. X-ray measurements: θ-scan (*a*), Φ-scan (*b*) and pole figure (*c*), and an SEM microphotograph (*d*) of the YBCO CC obtained after optimised pyrolysis and crystallisation conditions indicate good grain alignment and thin film morphology.

It was also found that the sample obtained from the CSD TFA-MOD sol-gel route by inkjet printing is superconducting (Fig. 5 a) with a sharp superconducting transition at 89.5 K and trapped magnetic field of 2.10 mT, which corresponds to a J_c of ~0.6 MA/cm^2 [5, 6]. Although the results for commercially available tapes produced by MOCVD (metalorganic chemical vapour deposition) (SuperPower, Fig. 5 *b*) are higher, with a trapped field of 16.21 mT and J_c of 1.6 MA/cm^2, it is likely that the performance to price ratio will become more attractive after complete further optimisation of the TFA-MOD process.

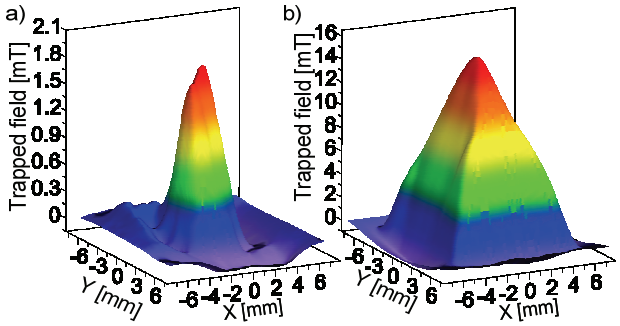

Fig. 5. Hall probe scans performed on YBCO tapes: a) obtained from the CSD metal TFA sol-gel route by inkjet printing; b) commercially available, produced by MOCVD (SuperPower).

The angular dependence of I_c in the MOCVD sample from SuperPower is presented in Figure 6. The peak I_c is shifted +6° from both +90° and -90°, suggesting a 6° angle between the c axis of the textured film and the normal to the substrate plane. The I_c is strongly dependent on rotation angle, and asymmetric about 0°, with a ratio of 2.4 between maximum and minimum I_c. In most applications, there is an off-axis (radial) field component and the maximum operating current is limited by this angular dependence. $I_c(\Phi)$ can be made much more isotropic, and the position and magnitude of the peaks controlled, by substitution (e.g. Gd) or the addition of other phases (e.g. $BaZrO_3$); and it has been demonstrated that this can be readily controlled in CSD routes [7]. The combination of this approach with inkjet printing is a key focus of ongoing research.

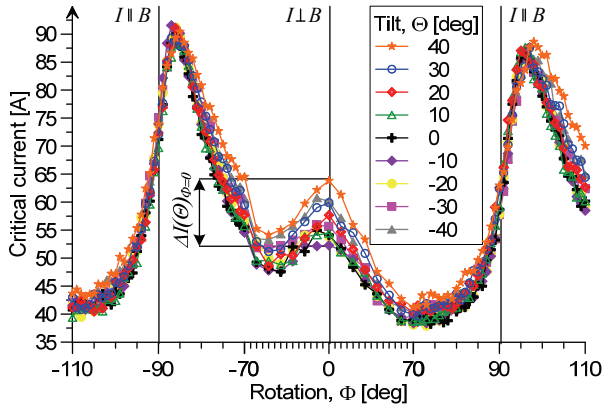

Fig. 6. The critical current dependence on rotation, Φ, at different tilts, Θ, at 77 K and 0.6 T. The spacing of minor tick marks on the rotation axis is 5°, and the range of rotation from -70° to 70° is shown at a reduced scale. The I_c peak is shifted +6° from ±90°, and minimum I_c occurs for a rotation angle of 70°.

Acknowledgments

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