

Low Cost Y-Ba-Cu-O Coated Conductors

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Abstract—Solution-based techniques have been examined as potential low-cost processes for manufacturing YBCO coated conductors. YBCO films prepared from metal trifluoroacetate precursors have achieved performance levels equaling or exceeding that of vapor deposited films with the same thickness on CeO₂/YSZ(sc) substrates. J_c's of 4.5 MA/cm² and 2 MA/cm² have been achieved in 0.4 μm thick YBCO films on CeO₂/YSZ(sc) and CeO₂/YSZ/CeO₂/Ni substrates, respectively. Textured Gd₂O₃ buffer layers have been deposited on deformation textured Ni substrates in a reel-to-reel process. The performance of YBCO films deposited on substrates containing the Gd₂O₃ seed layers is comparable in performance to YBCO films grown on all vacuum deposited buffer layers.

Index Terms—High temperature superconductors, epitaxial layers, YBaCuO.

I. INTRODUCTION

THE COMMERCIAL viability of the YBCO coated conductor will be determined in a large part by two key factors - performance and cost. Recent progress in the development of YBCO coated conductors has demonstrated the feasibility of preparing HTS conductors with a current density surpassing that of Bi-2223/Ag composite HTS conductors, particularly in a high magnetic field at liquid nitrogen temperature. However, many of the processes being developed for YBCO coated conductors are based on expensive, low rate, deposition techniques [1]–[3]. In contrast, the current price of a conventional Bi-2223/Ag composite conductor is approximately \$300/kA-m and is predicted to fall to approximately \$50/kA-m as manufacturing capacity increases [4]. Thus in order for YBCO coated conductors to be commercially competitive with the conventional Bi-2223 HTS conductor, industrial manufacturing processes must be developed that result in a

conductor price <\$50/kA-m and preferably <\$10/kA-m [5].

The importance of this price target for broad scale commercialization of the YBCO coated conductor technology is often not appreciated. It is common to focus attention on the higher field performance of YBCO at 77 K, which offers the unique promise of high-field magnets cooled with liquid nitrogen, something current Bi-2223 technology cannot attain. However, for major commercial applications, especially those in the power industry, closed-cycle-cooling systems, not requiring cryogen replenishment, are likely to be the norm. Such systems can be based on commercially available two-stage mechanical cryocoolers, which operate at temperatures down to 4 K. Since Bi-2223 conductors have good high-field performance below about 30K, Bi-2223 high field magnets cooled by cryocoolers can be - and have been - fabricated, operating at about 20 K [6].

We have focused efforts on developing low-cost solution-based routes for deposition of both the superconducting YBCO layer and the oxide buffer layers. Although solution-based processes have been developed for many applications, it is uncertain whether such low-cost processes can be developed for deposition of oxide layers over continuous lengths of metal substrates with the quality and uniformity required for HTS conductors. Our approach to answering this question is to characterize the solution-deposited oxide buffer and YBCO layers and to benchmark their performance against that of similar films prepared by conventional vapor deposition techniques.

In this paper, we review the current status of solution-based processes for the deposition of YBCO films and oxide buffer layers and compare their performance to films deposited by conventional vacuum-based deposition techniques.

II. EXPERIMENTAL

A. YBCO Deposition

The YBCO precursors were prepared as a stoichiometric solution of yttrium, barium and copper trifluoroacetates (TFA) using techniques similar to those described by McIntyre [7], [8]. The development of a solution-based deposition process for YBCO films was carried out on model substrates consisting of CeO₂/YSZ(sc). The CeO₂ layers, typically 20 nm thick, were deposited by rf magnetron sputtering. The YBCO precursor solutions were deposited by standard spin coating techniques.

Deposition of YBCO films on oxide buffered metal substrates was performed with the same precursor solution using either spin coating (short samples) or web coating (long length samples).

Processing of the YBCO films (0.4 μm) consists of two steps. The first is the decomposition of the precursor to a

Manuscript received September 18, 2000. This work was supported in part by the U.S. Department of Energy under Contract No. DE-FG02-97ER82324. and the U.S. Department of Air Force under Contract No. F336615-97-C-2728. The work at ORNL was sponsored by the U. S. Department of Energy, Office of Science, Division of Materials Sciences and the Office of Energy Efficiency and Renewable Energy, and was performed at ORNL managed by UT-Battelle, LLC for the USDOE under Contract No. DE-AC05-00OR22725.

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homogeneous film of CuO , Y_2O_3 and BaF_2 , which occurs between 150 – 400°C. The decomposition was carried out in either a continuous reel-to-reel or static oven, depending on the sample length. The second step is the formation of the YBCO phase, which is carried out in an $\text{O}_2/\text{H}_2\text{O}/\text{N}_2$ atmosphere at 700 – 850°C. Formation of the YBCO phase was carried out in a static furnace configuration.

B. Buffer Layer Deposition

Gd_2O_3 buffer seed layers were deposited on deformation textured Ni substrates using a gadolinium alkoxide precursor [9]. Precursor solutions were deposited on continuous lengths of Ni (up to 10 meters) using a laboratory web-coater. The precursor films were converted to the Gd_2O_3 phase under a H_2/Ar atmosphere at 900 – 1200°C using a continuous reel-to-reel process furnace.

Y_2O_3 and CeO_2 seed layers were deposited by e-beam deposition using techniques developed at Oak Ridge National Laboratory [10]. The YSZ barrier and CeO_2 cap layers were deposited by magnetron sputtering at either American Superconductor or Oak Ridge National Laboratory using techniques described previously [11]. The depositions were carried out on both static and reel-to-reel equipment.

C. Measurements

Current densities were determined by transport measurements at 77K in self-field with a criterion of $1\mu\text{V}/\text{cm}$. Measurements on metal substrates were made over the full width of the substrate, typically 5 – 10 mm. Measurements on single crystal substrates were made on ~ 1 mm wide bridges. Reel-to-reel xrd characterizations were carried out on a system developed at Oak Ridge National Laboratory. The oxide film thickness was determined using a Zygo interferometer or Rutherford Backscattering.

III. RESULTS AND DISCUSSION

A. Growth of YBCO Films on $\text{CeO}_2/\text{YSZ}(\text{sc})$ Substrates

The initial development of the solution-based process for YBCO film growth was carried out on model $\text{CeO}_2/\text{YSZ}(\text{sc})$ substrates. The use of the model substrate allowed us to investigate the inherent performance of the YBCO films independent of substrate quality. Most of the development effort on the single crystal substrates focused on a film thickness of $< 1\mu\text{m}$, which is easily accessible by spin coating techniques. Fig. 1 shows critical current density of YBCO films grown from the solution-based precursors as a function of film thickness. The performance of solution-deposited YBCO films closely matches that of comparable YBCO films deposited by vacuum techniques (i.e., pulsed laser deposition [12] or e-beam BaF_2 [13]) up to thickness of 1.1 μm . Beyond the 1 μm level, the J_c of the solution-deposited YBCO films decrease. This is associated with the appearance of a -axis oriented YBCO grains and the formation of second phases and porosity in the films. The reduced performance of the thicker films is believed to reflect the unoptimized process conditions and not an inherent limitation of the solution-based process. Similarly low performance was

initially obtained with the $< 1.0\mu\text{m}$ thick films before proper processing parameters were developed.

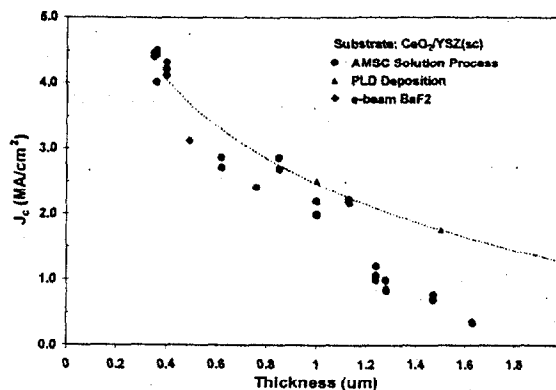


Fig. 1. Critical current density (77K, self-field) of YBCO films grown from a solution-based precursor on a $\text{CeO}_2/\text{YSZ}(\text{sc})$ substrate as a function of film thickness. Data for YBCO films deposited by PLD and e-beam BaF_2 are shown for comparison.

The reproducibility of the solution-based process was addressed by processing multiple samples and comparing the performance. Fig. 2 shows the measured J_c 's obtained on 3 separate bridges patterned on 4 individual YBCO films with a thickness of 0.4 μm . All films were processed under identical conditions. The data indicate an average J_c of $4.0 \pm 0.3\text{ MA}/\text{cm}^2$, demonstrating the inherent reproducibility of the solution-based process under controlled process conditions.

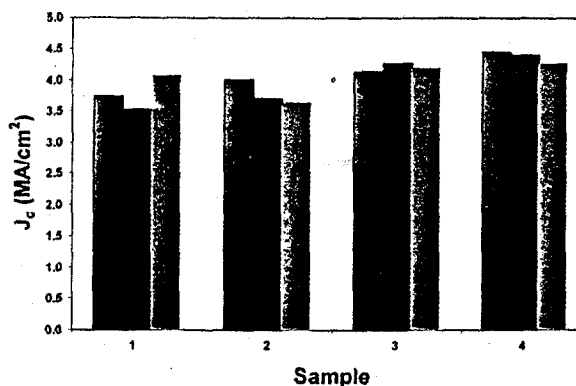


Fig. 2. Reproducibility of the critical current density (77K, self-field) of 0.4 μm YBCO films grown from a solution-based process on $\text{CeO}_2/\text{YSZ}(\text{sc})$ substrates. The J_c 's were measured on three individual bridges patterned on four separate samples.

B. Growth of YBCO Films on Oxide Buffered Metal Substrates

The compatibility of the solution-based YBCO deposition process with the metal substrates required for the YBCO coated conductors was tested using RABITS™ type substrates [14]. The substrates consisted of $\text{CeO}_2/\text{YSZ}/\text{CeO}_2/\text{Ni}$ obtained from Oak Ridge National Laboratory or $\text{CeO}_2/\text{YSZ}/\text{Y}_2\text{O}_3/\text{Ni}$ substrates prepared at American Superconductor. No statistical difference was found between substrates with CeO_2 or Y_2O_3 seed layers. The YBCO precursor solutions were deposited on short length samples ($< 1\text{ cm}$) by spin coating techniques and processed using the conditions established for the model substrates. X-ray

diffraction analysis of the films shows only the (00 l) reflections, indicating orientation of the YBCO c -axis perpendicular to the substrate surface. The films show a sharp superconducting transition, with transport J_c 's up to 2.0 MA/cm² (77K, self-field) obtained in 0.4 μ m thick films as shown in Fig. 3.

The variability of the YBCO films grown on the RABiTS™ type substrates is significantly larger than observed on the single crystal substrates and reflects primarily variability in the quality of the oxide buffered substrates.

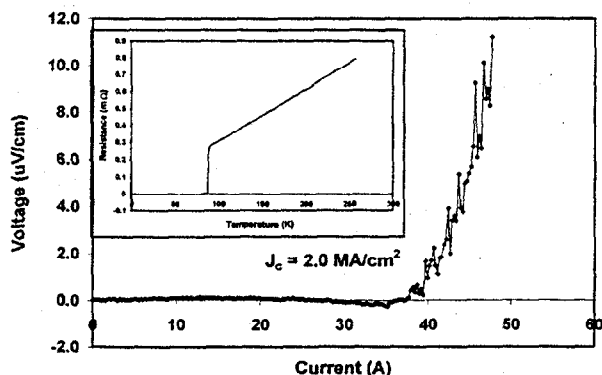


Fig. 3. I-V curve (77K, self-field) for a 0.4 μ m thick YBCO film deposited by a solution-based process on a CeO₂/YSZ/Y₂O₃/Ni substrate. Insert shows the superconducting transition.

C. Deposition of Gd₂O₃ Buffer Layers on Ni Substrates

The solution-deposition of oxide buffer layers has been demonstrated by Paranthaman on short length Ni substrates [9]. However, extending this technique to the manufacture of the YBCO coated conductors requires uniform texture, complete coverage and uniform thickness over the entire length and width of the metal tape substrate. The Gd₂O₃ layers were deposited on continuous lengths of 1-cm wide deformation textured Ni tape using a conventional web-coater. The x-ray diffraction (θ -2 θ) pattern of a 50-nm thick Gd₂O₃ film shows only the (00 l) reflections indicating the c -axis orientation of the Gd₂O₃ perpendicular with the Ni substrate [16].

Continuous x-ray diffraction measurements, made using a reel-to-reel xrd system, confirm the uniformity of both the in-plane and out-of-plane over a 7 meter length of Gd₂O₃/Ni tape as shown in Fig. 4.

Measurements of the thickness of Gd₂O₃ films, with a nominal thickness of 50 nm, show a variation of $\pm 10\%$ over the length of the tapes. Minimal variation is observed across the tape width.

These characterizations demonstrate the uniformity of the solution deposited Gd₂O₃ layers on long length Ni substrates. However to be useful for the YBCO coated conductor system, they must support the growth of additional buffer layers. To test the quality of the Gd₂O₃ seed layers, YSZ barrier layers (200 - 400 nm) and CeO₂ cap layers (~ 20 nm) were deposited on Gd₂O₃/Ni tapes by magnetron sputtering. The YSZ and CeO₂ depositions were done with both static and reel-to-reel systems.

Fig. 5 shows the x-ray diffraction spectrum (θ -2 θ) of the

full buffer stack. Sharp (00 l) reflections are observed with only a small peak associated with (111) texture, indicating the quality of the buffer layers. The corresponding θ -2 θ scan for a conventional all vacuum deposited CeO₂/YSZ/CeO₂/Ni buffer stack is included in Fig. 5 for comparison.

Fig. 6 shows the in-plane and out-of-plane texture measured along the length of the 1 meter tape using a reel-to-reel x-ray technique. Both the in-plane and out-of-plane textures of all three buffer layers are uniform along the length and are comparable to that of short length samples prepared in static deposition systems.

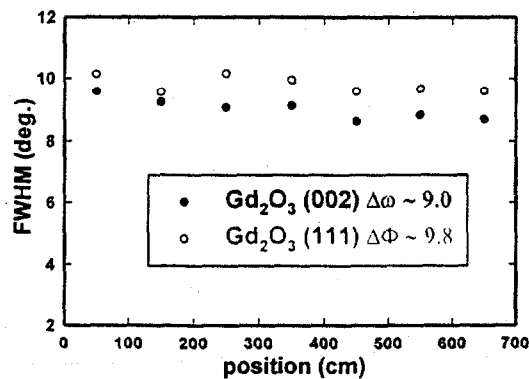


Fig. 4. Texture measurements obtained on a Gd₂O₃ buffer layer deposited by a solution process on a 7 meter length of deformation textured Ni tape.

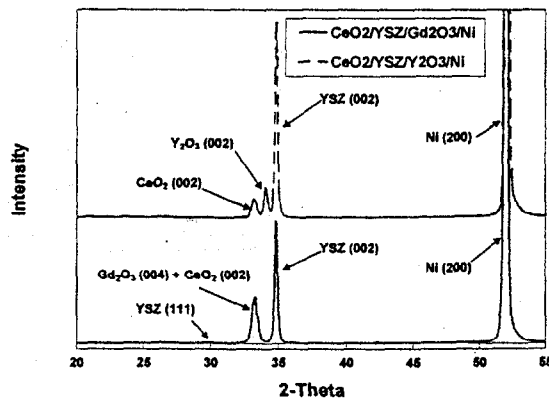


Fig. 5. X-ray diffraction patterns (θ -2 θ) showing the c -axis texture of an oxide buffered stack with the architecture CeO₂/YSZ/Gd₂O₃/Ni. The Gd₂O₃ layer was deposited by a solution-based process and the YSZ and CeO₂ layers were deposited by magnetron sputtering. Shown for comparison is the x-ray diffraction pattern of an oxide buffered stack with the architecture CeO₂/YSZ/Y₂O₃/Ni prepared entirely by vacuum deposition techniques.

D. Deposition of YBCO films on CeO₂/YSZ/Gd₂O₃/Ni Substrates

The final qualification of the solution deposited Gd₂O₃ buffer layers is the overall compatibility with the YBCO coatings. Fig. 7 shows the performance of a solution-deposited YBCO film on a CeO₂/YSZ/Gd₂O₃/Ni substrate. For comparison, the performance of a comparable YBCO film deposited on a CeO₂/YSZ/Y₂O₃/Ni substrate, with all buffer layers deposited by vacuum deposition techniques, is also included in Fig. 7. The performance of these two YBCO films is nearly identical, demonstrating the compatibility of solution-based deposition processes for the YBCO coated conductor.

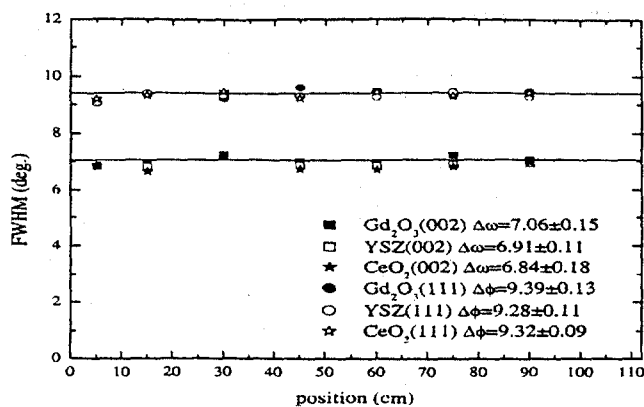


Fig. 6. Reel-to-reel x-ray diffraction scans showing the in-plane and out-of-plane texture of the oxide layers in the oxide buffer stack with the architecture $\text{CeO}_2/\text{YSZ}/\text{Gd}_2\text{O}_3/\text{Ni}$.

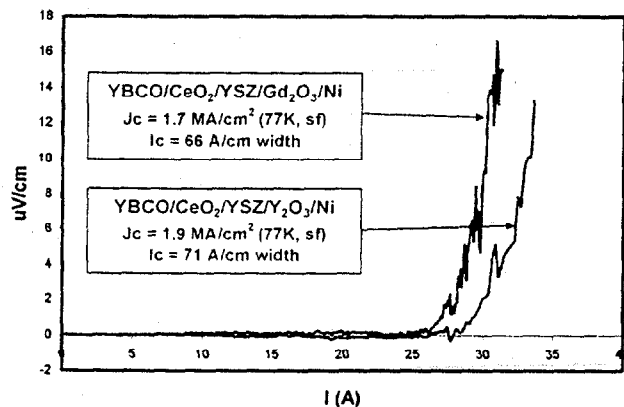


Fig. 7. I-V curves for $0.4 \mu\text{m}$ YBCO films deposited on $\text{CeO}_2/\text{YSZ}/\text{Gd}_2\text{O}_3/\text{Ni}$ and $\text{CeO}_2/\text{YSZ}/\text{CeO}_2/\text{Ni}$ substrates.

IV. SUMMARY

In this work, progress towards demonstration and development of key technologies necessary for the development of robust, high rate, low-cost deposition technologies for the YBCO coated conductors has been summarized. A solution-based process for the deposition for the YBCO films has achieved same performance level and reproducibility as previously only achieved in expensive vapor-based deposition techniques.

Although there has been significant progress in the development low-cost manufacturing technologies for select components of the YBCO coated conductors, key deposition technologies must still be improved. In addition, it is necessary to begin addressing the reproducibility of the deposition processes and to document the inherent variability associated with the long length manufacturing processes.

The successful development of these or similar low-cost technologies into robust manufacturing processes will be required in order for the YBCO HTS conductors to be economically competitive with the current Bi-2223 conductors in the broad commercial HTS market.

ACKNOWLEDGMENT

The authors wish to thank M. Cima, J. Smith, M. Gopal, and L. Rigione of MIT for their on-going contributions to this

work. The authors also acknowledgment the financial support of the Pirelli, the Electric Power Research Institute, the U.S Air Force and the U.S, Department of Energy.

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