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Final Report on CRADA ORNL05-0703

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Prepared by
David K. Christen
Group Leader, Superconductive and Energy Efficient Materials
Materials Science and Technology Division

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David K. Christen

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ABSTRACT

The work of this CRADA has been focused on the development of Rolling-Assisted Biaxially Textured Substrate (RABiTS)-based high-temperature superconducting (HTS) coated conductor technology that is in the pre-commercial development stage. Metal-Oxide Technologies, Inc. (MetOx) is a Houston-based small business that is developing and manufacturing second-generation (2G) HTS wire using an all-Metallo-Organic Chemical Vapor Deposition (MOCVD) process, including the buffer layers and HTS coating. Advances toward commercialization were enabled by coordinated interactions that facilitated the synthesis, characterization, and iterative optimization of prototype 2G wire segments.

1. OBJECTIVES

The project tasking was designed to help MetOx optimize their approach to 2G conductors.[1] Since their technology is based on the ORNL-developed RABiTS concept,[2,3] ORNL was well-positioned to provide expertise, materials, and analytical services to enable MetOx to iteratively refine and develop its fabrication processes. The objective was to interactively evaluate the HTS films and buffer layers that can be achieved using MetOx proprietary processes. During the course of this CRADA, the parties synthesized and characterized epitaxial films of $YBa_2Cu_3O_7$ (YBCO) and various proprietary and non-proprietary buffer layers deposited on RABiTS or other flexible, textured templates utilizing the MetOx proprietary MOCVD process and other existing intellectual property. Characterization was aimed at validating the material science and technology associated with the MetOx intellectual property, thereby advancing the commercialization of high temperature superconductors for electric power or other commercial applications. It was not the intent of this project to develop new intellectual property, materials, processes or equipment. Nor was it the intent to modify the existing intellectual property, YBCO films, buffer layers, or any of the processes, materials, or equipment used to create such films.

Specific tasks and objectives may be itemized as the following:

- ORNL supplied few-meter lengths of fully buffered Ni-W-based RABiTS for MetOx deposition of the HTS coating, as a means to compare to results obtained on MetOx buffered textured metal tapes.

- ORNL measured magnetic field, temperature and orientation dependent superconducting properties of MetOx YBCO samples, with analysis that provides separation of the inter- vs. intra-grain critical current density

- ORNL supplied to MetOx treated Ni-W textured tapes to provide the two-dimensional ordered surface nanostructure of sulfur atoms that enables epitaxial growth of oxide buffer layers

- ORNL provided visualization, compositional analysis and interpretation of the material micro- and nano-structure through cross-sectional studies of MetOx tapes using Scanning and Transmission Electron Microscopy (SEM and TEM).

2. BENEFITS

The project general goal of establishing an internationally competitive U.S. HTS industry, targeted to power-intensive commercial applications, benefits the mission of the DOE Office of Electricity Delivery and Energy Reliability, which is to lead national efforts to modernize the electric grid; enhance security and reliability of the energy infrastructure; and facilitate recovery from disruptions to energy supply.

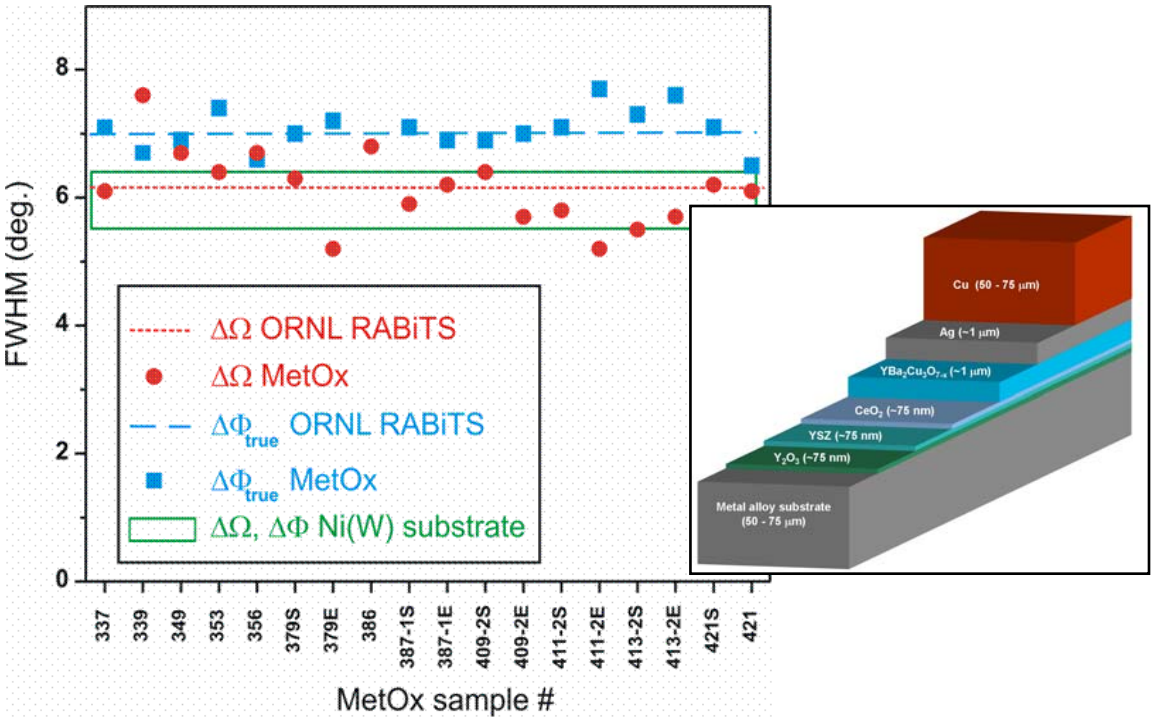

Fig. 1. A comparison of buffer crystallinity for 18 MetOx samples. The crystallinity of MetOx Y_2O_3 single buffer layer is comparable to that of an ORNL RABiTS buffer, and to the texture of the underlying Ni(W) substrate. The inset is an example of a RABiTS structure, where the buffer-layer stack of oxide layers can be adjusted and tailored for a particular 2G wire approach.

3. WORK PERFORMED

An early goal was to establish that MetOx could produce functional buffer layers using their MOCVD process for deposition on ORNL textured metal tapes. MetOx was able to show achievement of good texture in buffer layers based on yttrium oxide deposited on Ni3%W, as shown in Fig. 1. Moreover, the approach was naturally scalable to provide deposition over long lengths of tape.

The deposition of MetOx YBCO coatings on these substrates identified several problems associated with both the buffer layers and the YBCO depositions. This was documented by comparison of superconducting properties of MetOx HTS coatings on both ORNL RABiTS and MetOx buffered tapes. For example, it was found that high deposition temperatures resulted in

excessive formation of NiO beneath both the ORNL and MetOx buffer layers, with the associated problem of crack formation. However, in the initial stages, MetOx was able to produce YBCO coatings with critical current density, J_c, of nearly 1.5 MA/cm^2, which showed proof-of-principal for the overall approach.

As part of the systematics, MetOx provided a representative sampling of process parameterized samples for measurements at ORNL of the superconductive properties, with information to be fed back for iterative optimization. The measurements included the superconducting transition temperature, T_c, the magnetic field-dependent J_c at liquid nitrogen temperature, 77 K, and the dependence of J_c on orientation of the material in an applied magnetic field. The latter is an important property because the HTS fundamental superconductive properties are highly anisotropic due to the layered cuprate crystal structure and the related effects on electronic structure.[4] The manner in which J_c varies with orientation of the material in field is relevant to applications, since tape segments in any application may experience different field directions at different geometrical locations in the device (e.g., segments of tape in a transmission cable or coil of a motor, transformer, etc.). Some representative results of J_c vs. orientation are shown in Fig. 2, where it was found that the MetOx materials exhibit qualitatively standard behavior. Here, J_c is maximum for field parallel to the cuprate planes (plane of the tape) and shows a broad plateau for fields oriented in an angular range near the tape normal (i.e., H||YBCO c-axis). In theory, this type of behavior reflects the electronic supercarrier mass anisotropy, which for pinning by scalar, isotropic defects, would scale as a function of an effective magnetic field given by $H_{eff}(\theta) = \varepsilon(\theta)\, H$,[4] where

$$\varepsilon(\theta) = \left[\sin(\theta)^2 + \frac{m_{ab}}{m_c} \cos(\theta)^2 \right]^{\frac{1}{2}}, \text{ and for YBCO, } \frac{m_{ab}}{m_c} \cong .03 - .04 .$$

In Fig. 2, the pronounced peak near H || tape plane (θ=0) is probably due to the combination of a minimum H_{eff} due to electronic anisotropy above, and the presence of planar interlayer second-phase defects, which is common in YBCO and is known to provide strong flux pinning.

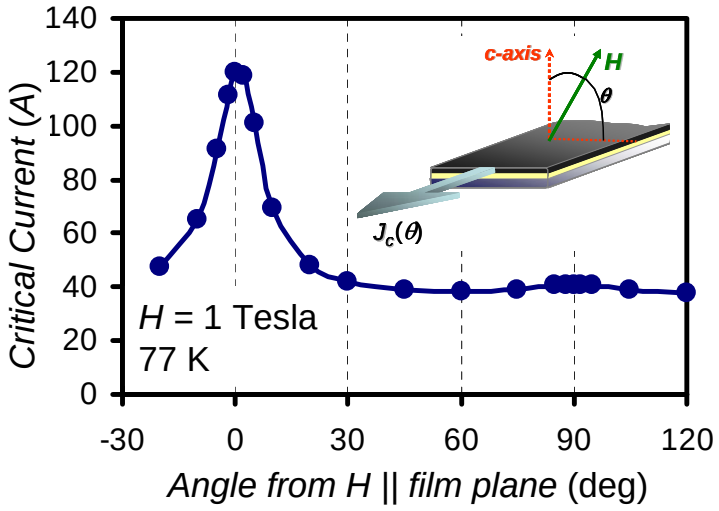

Fig. 2. The dependence of J_c on material orientation in a magnetic field of 1 Tesla at 77 K, for a MetOx tape that had an critical current of 175 A/cm-width in self-field.

Since the entire 2G approach to conductors is aimed at mitigating the deleterious current-limiting effects of inter-grain misorientations (the grain-boundary "weak-link" problem), it is important to assess the relative limitations on the total current that is posed by the grain-boundaries vs. the crystalline grains. We conducted a series of magnetic measurements that were aimed at separating the inter-grain and intra-grain critical currents on a set of MetOx 2G prototypes. The general theory for this approach was developed by a group at CSIC Barcelona, and involves a prescribed measurement protocol.[5] Examples of results are shown in Fig. 3. In these studies, the magnetic moment of Fig. 3(a) is caused by induced supercurrents in the material, so that the model can relate features in the magnetic moment's field dependence to the inter-grain and intra-grain J_c values, $J_{c,GB}$ and $J_{c,G}$, respectively. It is seen in Fig. 3(b) that the low-field J_c are indeed limited by the inter-grain conduction. At the time of this study, the best properties were obtained by MetOx by deposition on the ORNL-buffer layers, which scale more toward the ideal case of $J_{c,GB} = J_{c,G}$. Since in some cases the intra-grain J_c values shown here at 50 K were quite good, and the result of overall $J_c \approx$ 1.5 MA/cm^2 on isolated sample, MetOx had established feasibility of attaining good superconductive properties by the MOCVD of the YBCO layer.

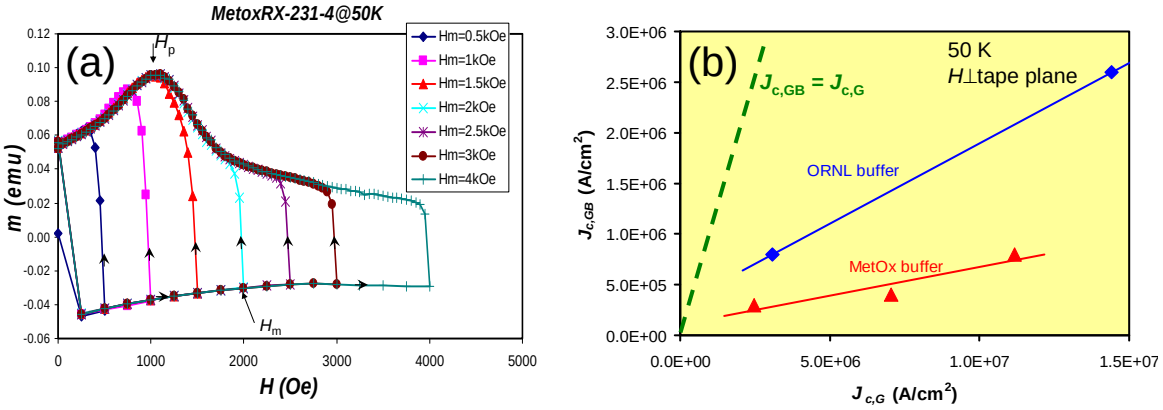

Fig. 3. (a) An example of the magnetic measurement protocol. Loops to successively higher fields are probed, until a field H_m is identified, whereby higher field excursions produce no further change in the field peak position, H_p, of the magnetic moment. (b) Results at 50 K showing the inter-grain vs. intra-grain critical current densities, $J_{c,GB}$ and $J_{c,G}$, respectively.

Further work then focused on refining the deposition by MOCVD of buffer-layer architectures by employing either double or triple thin film layers to decrease oxygen diffusion to the nickel alloy and cation diffusion to grain boundaries in the YBCO. In addition, MetOx secured its own source of crystalline-textured Ni-5%W tape. Previously, ORNL had shown that the epitaxial growth of most oxide buffer materials is best assured by a special pre-treatment of the metal surface.[6] In short, this thermal treatment in the presence of H_2S gas produces a self-assembled sulfur monolayer superstructure, designated "*c*(2x2)," on the metal surface, whereby every other hollow between surface Ni or W atoms is occupied by a sulfur atom. The structure is stable to temperatures of typical buffer layer depositions, and effectively catalyzes the initial atomic order of the buffer oxygen and cations on the surface, as shown schematically in Fig. 4. As part of the CRADA, ORNL provided this heat treatment process to textured tapes from MetOx, and transferred the knowledge base for this procedure. In the course of the CRADA, ORNL treated approximately 85 m of MetOx tapes.

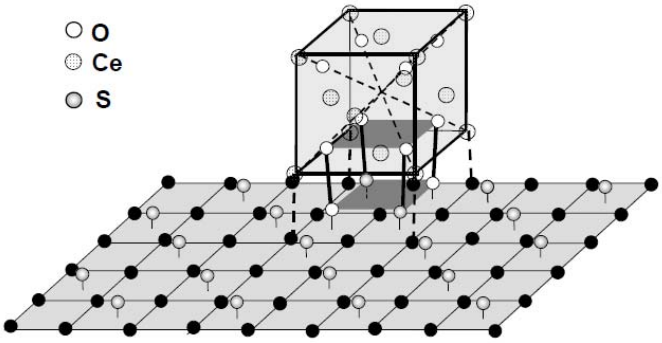

Fig. 4. Proposed c(2×2) superstructure-mediated epitaxial growth of CeO_2 on (001) Ni-alloy surface. The superstructure S adatoms become constituents of the basal oxygen sublattice of CeO_2.

In order to assess the effects of buffer layer architecture and structure, ORNL provided high-resolution cross-section SEM and TEM measurements on selected all-MOCVD samples prepared by MetOx. The resulting correlations among superconductive properties and observed microstructure helped guide optimization of the overall MetOx all-MOCVD approach. Examples of the some distinctions in the microstructure of differently processed materials are shown in Fig. 5, which are Z-contrast scanning TEM images of two samples from MetOx.

In this case, additional elemental mapping (not shown) revealed that the YBCO grown on single buffered tapes show a higher density of YCuO and CuO precipitates within the YBCO grains. The additional YBCO that grows over these precipitates show larger crystallographic tilts, which could act as current blocking paths, as exemplified by the differences in J_c of two samples, 0.4 MA/cm^2 for single-layer buffer compared to 1.27 MA/cm^2 for the multi-layered. The single-buffer samples also exhibit a rougher YBCO/Y_2O_3 interface than that on the multilayer buffers that had Y_2O_3 as a cap buffer layer.

Although the single-buffer sample shows a somewhat thicker reaction layer of NiO and Ni-W-O at the interface between the Ni-W tape and the buffer layer, in both cases the buffers are adequate oxygen and Ni barriers since no Ni is observed to diffuse into the overlayers. In addition, the overall YBCO matrix composition is the same in the two samples.

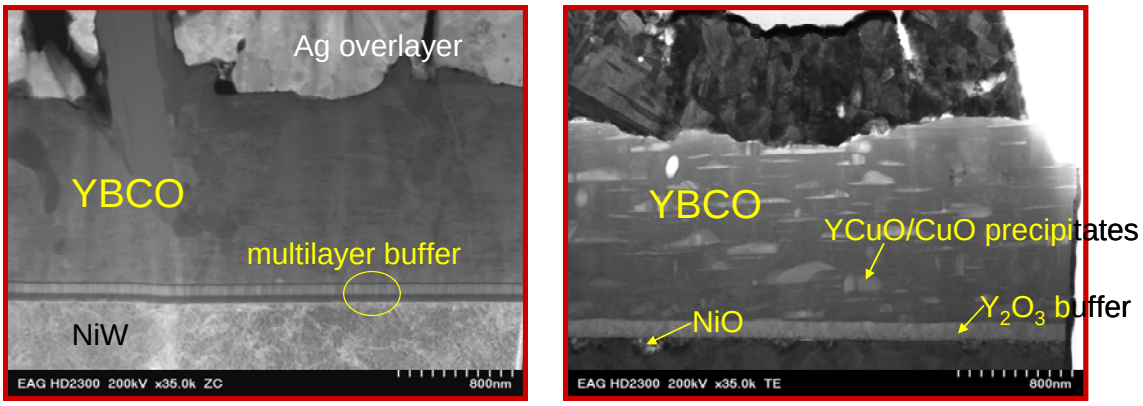

Fig. 5. Z-contrast scanning TEM images of two MetOx samples. (a) Three-layer buffer architecture. YBCO with J_c = 1.3 MA/cm^2. (b) Single-buffer architecture with YBCO J_c = 0.4 MA/cm^2.

In all, ten MetOx samples were investigated by either SEM or TEM, with the general conclusion that the buffer combination seems to provide improved YBCO properties compared to the single buffer approach, the latter of course being preferred because of simplicity and cost reduction. Subsequent development of the multilayer buffer architecture has led to significant YBCO performance improvements, yielding J_c = 2.13 MA/cm^2, corresponding to a current level of I_c = 236 A/cm-width.

4. CONCLUSIONS

The CRADA project has advanced the all-MOCVD approach to 2G superconducting wires that MetOx pursues. These results have helped MetOx make iterative modifications in processing in progressing toward optimized HTS coatings, and in moving toward self-sufficiency in the production of the entire coated conductor. The work has pointed to future objectives, which in part will be supported through continued collaborative interactions between MetOx and ORNL.

ORNL will continue to provide assistance in areas that have been identified by MetOx as needed for further progress. These will include the following:

- Further microstructural characterization to help MetOx optimize their buffer and HTS materials
- Reel-to-reel x-ray diffraction characterization as MetOx advances toward production of longer lengths
- Superconductive properties characterization of $J_c(H,T,\theta)$ on emerging prototypes, as needed by MetOx

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