Title: A COMPARISON OF BUFFER LAYER ARCHITECTURES ON CONTINUOUSLY PROCESSED YBCO COATED CONDUCTORS BASED ON THE IBAD YSZ PROCESS

Author(s): Terry G. Holesinger, MST-STC
Steven R. Foltyn, MST-STC
Paul N. Arendt, MST-STC
Quanxi Jia, MST-STC
Paul C. Dowden, MST-STC
Ray F. Depaula, MST-STC
J.R. Groves, MST-STC


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A Comparison of Buffer Layer Architectures on Continuously Processed YBCO Coated Conductors Based on the IBAD YSZ Process

Terry G. Holesinger, Steven R. Foltyn, Paul N. Arendt, Quanxi Jia, Paul C. Dowden, Raymond F. DePaula, and James R. Groves

Abstract—The microstructures of continuously processed YBa$_2$Cu$_3$O$_y$ (YBCO) coated conductors processed with three different architectures are presented. YBCO films were deposited directly on ion-beam-assisted deposition (IBAD) yttria-stabilized zirconia (YSZ) or on intervening layers of Y$_2$O$_3$ or CeO$_2$. Different interfacial reactions were observed in each case. The volume changes that occur with the interfacial reactions were calculated based on the identified reaction products. The calculated volume changes correlate with the observed microstructures and appear to be an important factor in determining an optimal buffer layer system. The interfacial reactions do not preclude the attainment of high $I_c$ and $J_c$ values in these coated conductors.

Index Terms—coated conductor, IBAD, TEM, YBCO

INTRODUCTION

Coated conductors require a biaxially textured template upon which YBa$_2$Cu$_3$O$_y$ (YBCO) can be grown epitaxially. The highest critical currents ($I_c$) and current densities ($J_c$) achieved in one-meter lengths have been obtained on textured templates consisting of ion-beam-assisted-deposition (IBAD) of biaxially textured, yttria-stabilized zirconia (YSZ) buffer layers on nickel-alloy metal substrates [1]. Subsequent buffer layer(s) and YBCO were deposited by pulsed laser deposition (PLD) [2, 3].

The IBAD YSZ layer provides the biaxially aligned template for oriented growth of subsequent layers [4, 5] and acts as a diffusion barrier to prevent constituents of the metallic substrate from substituting into the YBCO film and degrading its superconducting properties [6]. YBCO may be deposited directly onto the IBAD YSZ film. However, additional buffer layers such as CeO$_2$, appear to be necessary for optimizing the transport properties of the YBCO film. The second buffer layer may provide a better lattice match to YBCO [7] or improve the chemical stability of the interface relative to the high reactivity of barium in YBCO [8].

Understanding the interactions between the YBCO and the underlying buffer layers is important for developing coated conductors into a practical conductor technology. CeO$_2$ is a stable oxide with a good lattice match to YBCO and it has been successfully used as a buffer layer [9-11]. However, recent work by Holesinger et al. showed that even this highly stable material reacts with YBCO along the interface [12]. Since it appears that nearly all materials react with YBCO at typical processing temperatures, it is especially important to understand what general aspects of the interfacial reactions between a given material and YBCO limit or enhance the rate of reaction. The current work will document the salient features of the microstructure in YBCO coated conductors comprised of three different architectures; (1) YBCO / IBAD YSZ / Inconel 625, (2) YBCO / Y$_2$O$_3$ / IBAD YSZ / Inconel 625, and (3) YBCO / CeO$_2$ / IBAD YSZ / Inconel 625.

EXPERIMENTAL

IBAD YSZ provides the biaxially textured template for the samples in this study on Inconel 625 substrates. The YBCO is deposited directly onto the YSZ or onto an intervening layer of Y$_2$O$_3$ or CeO$_2$. The YBCO, Y$_2$O$_3$, and/or CeO$_2$ were all deposited by pulsed laser deposition (PLD). The thickness of the YBCO coating varied from 1 to 3 microns. The IBAD YSZ thickness was kept at 0.5 μm and the additional layers of Y$_2$O$_3$ or CeO$_2$ were kept at a thickness of 300 nm. Additional details can be found elsewhere [1-3]. The transport properties of the continuously processed, coated conductors are shown in Table I.

Transmission and scanning electron microscopy (TEM and SEM) samples were prepared in the same manner for viewing in the longitudinal transverse direction (perpendicular to both the nominal c-axis of the film and direction of current flow). Samples were cut and glued between two pieces of silicon.

TABLE I

<table>
<thead>
<tr>
<th>Architecture</th>
<th>$I_c$ (MA/cm$^2$)</th>
<th>$I_c$ (A) $^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO / IBAD YSZ</td>
<td>≤ 0.7</td>
<td>≤ 100</td>
</tr>
<tr>
<td>YBCO / Y$_2$O$_3$ / IBAD YSZ</td>
<td>≤ 1.0</td>
<td>≤ 120</td>
</tr>
<tr>
<td>YBCO / CeO$_2$ / IBAD YSZ</td>
<td>≤ 1.0</td>
<td>≤ 200</td>
</tr>
</tbody>
</table>

$^\dagger$ All of the substrates were 1 cm wide. Hence, the $I_c$ values in amps directly translate into A/cm-width.

The samples were mounted in 3 mm non-magnetic stainless steel tubes, sliced, dimple-polished, and then ion-milled to electron transparency. Phase identification was performed by energy dispersive spectroscopy (EDS) and electron diffraction.

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T.G. Holesinger is with the Los Alamos National Laboratory, Los Alamos, NM 87545 USA (telephone: 505-667-2911, e-mail: holesinger@lanl.gov).

S.R. Foltyn, P.N. Arendt, Q.X. Jia, P.C. Dowden, R.F. DePaula, and J.R. Groves are with the Los Alamos National Laboratory, Los Alamos, NM 87545 USA.
RESULTS

A. Transport properties

Table I contains the specifics on the architecture and transport properties of the samples examined in this study. The best results in terms of transport properties were obtained with an additional CeO$_2$ buffer between the IBAD YSZ and YBCO. The poorest performing samples were those in which the YBCO was deposited directly onto the IBAD YSZ. The absolute performance in terms of current/cm-width of any given sample is a function of both the YBCO thickness and its J$_c$. The best result of 100 A/cm-width with YBCO directly deposited onto the IBAD YSZ was obtained with a YBCO film thickness of around 1.5 μm and a J$_c$ value of 0.67 MA/cm$^2$. In contrast, the best result with using an additional CeO$_2$ buffer layer on top of the IBAD YSZ was a J$_c$ value of 1 MA/cm$^2$ in a 2 μm thick film and a measured I$_c$ of 200 A in a one cm wide tape. In order to reliably manufacture high-current YBCO coated conductors (I$_c$ > 200 A/cm-width), one must maintain a high J$_c$ value as the thickness of the YBCO film is increased. As will be shown below, the choice of the architecture of the coated conductor plays an important part in obtaining high performance YBCO coated conductors.

B. YBCO / IBAD YSZ

Shown in Fig. 1a and b are TEM cross-sections of a YBCO film that was directly deposited onto an IBAD-YSZ template. The lattice mismatch between YSZ and YBCO is $\Delta a/a = -5.67\%$. The defects found along the interface were porosity and interfacial reaction phases. The identified reaction products were BaZrO$_3$, Y$_2$BaCuO$_5$ (Y-211), and CuO. The reaction can be written as follows:

$$3\text{ZrO}_2 + 2\text{YBa}_2\text{Cu}_3\text{O}_7 \rightarrow$$

$$3\text{BaZrO}_3 + \text{Y-211} + 5\text{CuO} + (1/2)\text{O}_2 \quad (1)$$

Associated with the interfacial reaction is a volume change of -0.9%. The negative volume change correlates with the interfacial porosity that was found. The interfacial reaction resulted in a continuous layer of BaZrO$_3$ and intermittent particles of Y-211 and CuO. The composites of the reaction phases were found to extend up to 0.25 μm into the film from the interface.

C. YBCO / Y$_2$O$_3$ / IBAD YSZ

Higher J$_c$ and I$_c$ values were obtained in continuously processed YBCO coated conductors when an intermediate buffer layer of Y$_2$O$_3$ was inserted between the IBAD YSZ and YBCO films. The lattice mismatch between Y$_2$O$_3$ and YBCO is $\Delta a/a = -2.67\%$. Shown in Fig. 2a and b are two examples of coated conductors with this architecture. The difference between the two samples is the porosity found in the sample of Fig. 2a. The reaction phases identified in these samples were Y-211 and CuO. The reaction can be written as follows:

$$3\text{Y}_2\text{O}_3 + 2\text{YBa}_2\text{Cu}_3\text{O}_7 \rightarrow$$

$$4\text{Y-211} + 2\text{CuO} + (1/2)\text{O}_2 \quad (2)$$

Associated with the interfacial reaction is a volume change of -6.7%. As is evident from Fig. 2, interfacial porosity in these samples did not always occur despite the significant negative volume change that occurs during the reaction. The latter observation suggests another aspect to this particular reaction that is not entirely understood at this point. One possibility, as suggested by the difference in the morphology along the interfaces of the samples shown in Fig. 2, is the point during processing when the Y-211 forms. Diffraction analysis of the structure revealed an orientational relationship of [001]$_{YSZ}$ || [001]$_{Y211}$ || [001]$_{Y123}$ and (110)$_{YSZ}$ || (010)$_{Y211}$ || (010)$_{Y123}$. A reverse sequence of events is suggested by the microstructure of Fig. 2a. The formation of porosity in samples of the type shown in Fig. 2a did correlate with a small fraction of a-axis growth of the YBCO and somewhat lower J$_c$ values. In any case, the underlying mechanism that determines which microstructure forms has not been completely determined at this point.

Shown in Fig. 3 is a higher-magnification of the reaction between the YBCO and Y$_2$O$_3$. In this particular case, the reaction did not consume the entire Y$_2$O$_3$ film. In no instance did any reaction proceed past the Y$_2$O$_3$ / IBAD YSZ interface.
Fig. 2: TEM micrographs of YBCO coated conductors manufactured with a 30 nm YSZ buffer layer between the YBCO and IBAD YSZ. In (a) a significant amount of porosity is seen along the interface in addition to the interfacial reaction phases of Y-211 and CuO. In (b), little porosity is found and the Y-211 forms a semi-continuous layer along the interface. The film thickness and $J_c$ values for tapes are (a) 1.5 μm and 0.67 MA/cm$^2$ and (b) 1 μm and 1.0 MA/cm$^2$. Both 1 cm-wide tapes carried 100 A of current in self-field at 75 K.

The time at temperature for the deposition of the YBCO determines in part the amount of interfacial reaction that occurs. Fig. 4 contains a micrograph of a sample with a 0.2 μm YBCO coating on an intermediate Y$_2$O$_3$ buffer layer on IBAD YSZ. In this case, no reaction along the interface between the YBCO and Y$_2$O$_3$ was observed. The time at the deposition temperature for the latter sample was 2 min. In contrast, the thicker YBCO films of the continuously processed tapes were at the deposition temperature for 6 min. The later film was also deposited at a higher deposition rate.

At lower deposition temperatures, the processing of thick YBCO films still resulted in the formation of interfacial reaction phases. As shown in Fig. 5, porosity, Y-211, and CuO could still be found in this film which was deposited at 650°C. The film was not superconducting above 75K and shows that the interfacial reaction phases do not preclude the attainment of high $I_c$, $J_c$ coated conductors. Other factors associated with the film deposition have a bigger role in determining the transport properties. In the example shown here, the lower deposition temperature resulted in the formation of a large fraction of a-axis oriented grains as indicated in Fig. 5.

D. YBCO / CeO$_2$ / IBAD YSZ

The best combination of thick YBCO films and high $J_c$ values were obtained in continuously processed YBCO coated conductors containing an intermediate buffer layer of CeO$_2$ between the IBAD YSZ and YBCO films. The lattice mismatch between CeO$_2$ and YBCO is ~0.67%. The microstructure of this system is shown in Fig. 6. The reaction phases identified in these samples were BaCeO$_3$, YCuO$_2$, and CuO. The reaction can be written as follows:

\[
\begin{align*}
(2)CeO_2 + YBa_2Cu_3O_7 & \rightarrow \\
(2)BaCeO_3 + YCuO_2 + (2)CuO + (1/2)O_2
\end{align*}
\]  

(3)
Associated with the interfacial reaction is a volume change of +7.6%. A noticeable difference exists between this architecture and the previous two in the extent of the reactions involved. In contrast to the preceding two examples, most of the CeO₂ layer remained intact with only isolated interfacial reactions. The localized reactions between the CeO₂ and YBCO resulted in a two-phase structure in which YCuO₂ lies above the BaCeO₃ relative to the interface as shown in Fig. 7. This defect structure was found to extend up to 0.25 μm into the YBCO film. In no instance was any reaction between the CeO₂ and YBCO observed to extend beyond the IBAD YSZ / CeO₂ interface.

E. Excess Material from Interfacial Reactions

In some instances, an interfacial reaction will proceed without the formation of all reaction products listed in (1), (2), or (3). In these cases, excess material is carried away from the interface and intercalated into the YBCO film in the form of Y₂Ba₃Cu₄Oₓ (Y-247), YBa₂Cu₃Oₓ (Y-124), or Y₃Ba₂Cu₄Oₓ (Y-224) [12, 13]. Shown in Fig. 8 is an example from the samples containing an intermediate CeO₂ layer. An isolated grain of BaCeO₃ lies at the base of a grain boundary in the YBCO film. Extending from this grain boundary are basal-plane intergrowths in the YBCO. The penetration distance of the intergrowth is inversely proportional to the distance from the interface.

DISCUSSION

The results for the three systems examined are summarized in Table II. All of the different buffer layers reacted to some extent with YBCO during processing. Hence, an optimization of the superconducting properties requires more than just a consideration of the lattice match between the buffer layer and YBCO. The choice for a buffer layer next to YBCO depends on how the reactions between them change the interfacial microstructure. Based on the data shown, an important consideration is the volume change associated with

<table>
<thead>
<tr>
<th>Architecture</th>
<th>Reaction Phases</th>
<th>Volume Change</th>
<th>Lattice Mismatch</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO/IBAD YSZ</td>
<td>BaZrO₃, Y-211, CuO</td>
<td>-0.9%</td>
<td>-5.67%</td>
</tr>
<tr>
<td>YBCO/Y₂O₃/IBAD YSZ</td>
<td>Y-211, CuO</td>
<td>-6.7%</td>
<td>-2.67%</td>
</tr>
<tr>
<td>YBCO/Y₂O₃/IBAD YSZ</td>
<td>BaCeO₃, YCuO₂, CuO</td>
<td>+7.6%</td>
<td>-0.67%</td>
</tr>
</tbody>
</table>

* Interfacial reaction phases formed from reaction with YBCO.
* Change in volume that occurs when YBCO reacts with the buffer layer.
* Lattice mismatch between the buffer layer and YBCO, (a-b)/b*100 where a is the average between a and b lattice parameters of YBCO and b is the lattice parameter of the buffer layer.
the reactions. Reactions that result in a positive volume change are localized whereas those that result in a negative volume change tended to be more extensive and result in interfacial porosity. Since the reactions generally occur after the nucleation and growth of the YBCO film has begun, there can be a space limitation for reactions that result in positive volume change. This appears to be the case for the CeO$_2$ buffer layers. Exceptions to this effect can be found. With the Y$_2$O$_3$ buffer layers, it appears that in some cases, the reaction between the buffer layer and YBCO can occur before nucleation and growth of the superconducting film. The conditions under which this occurs are not understood at this point. However, it appears that the YBCO film was able to orient itself on the Y-211 reaction phase in this particular case.

Other factors affecting film development are the deposition temperature, the time for processing at temperature, and incomplete interfacial reactions. In the example of Fig. 5 shown above with the Y$_2$O$_3$ buffer layers, lowering the processing temperature resulted in the formation of a-axis YBCO grains in the film. However, the lower processing temperature did not inhibit the interfacial reaction between the buffer and YBCO. On the other hand, the interfacial reactions can be minimized at normal processing conditions by limiting the time at the deposition temperature. This is illustrated by the sample shown in Fig. 4. The latter example also illustrates the more general case in which the nucleation and growth of the YBCO film occurs before the reaction products form. A significant number of intergrowths were found in the YBCO film that were related to the incomplete formation of the reaction products along the interface [12]. In the example of Fig 8, the lone formation of BaCeO$_3$ does not satisfy the mass balance of (3). Hence, the excess material from the reaction must be accounted for in some form. The presence of the intergrowths emanating from the grain boundary would satisfy this mass balance if the excess material from the reaction incorporates itself into the YBCO films as intergrowths. The identified intergrowths of Y-247, Y124, and Y-224 that occur are consistent with the need to place excess Y and Cu from the incomplete reaction between CeO$_2$ and YBCO.

In spite of the fact that interfacial reactions were found in all of the continuously processed samples, it did not preclude the attainment of high $I$ and $J_c$ YBCO coated conductors. In fact, high $I$ conductors could be obtained in all of the sample architectures used. It is true that the absolute performance of the coated conductor was determined by the choice of the buffer layer next to the YBCO film. It is speculated that the reaction products form a dead layer along the interface and reduce the cross section for current transport [14]. In this respect, CeO$_2$ performed best in improving the chemical stability of the interface relative to the high reactivity of Ba and minimizing interfacial reactions that ultimately reduce the transport properties of the films.

**SUMMARY**

The microstructures of continuously processed YBa$_2$Cu$_3$O$_y$ (YBCO) coated conductors were investigated with respect to the interfacial reactions that occur between the YBCO and the underlying buffer layer. YBCO films were deposited directly on IBAD YSZ or on intervening buffer layers of Y$_2$O$_3$ or CeO$_2$. Different interfacial reactions were observed in each case. However, the interfacial reactions did not preclude the attainment of high $I$ and $J_c$ values in these continuously-processed coated conductors. The volume change associated with a given interfacial reaction appears to affect the extent and morphology of the reactions between the thick YBCO films and the underlying buffer layer. Those with a negative
Fig. 8: TEM micrograph showing the intergrowths emanating from the the grain boundary. At the base of the grain boundary is an isolated BaCeO$_3$ resulting from the reaction between CeO$_2$ and YBCO. Excess yttrium and copper from this reaction diffuse along the grain boundary and intercalate into the YBCO film as intergrowths of the Y-247, Y-124, or Y-224 phases rather than forming the other secondary phases from the reaction, YCuO and CuO.

volume change tended to result in interfacial reactions that covered most, if not all, of the interface between the buffer layer and the thick YBCO film. This was the case for YBCO deposited on YSZ or Y$_2$O$_3$. The reaction between CeO$_2$ and YBCO results in a positive volume change and the reactions between CeO$_2$ and YBCO were localized. The highest critical currents of 200 A in the continuously-processed, coated conductor were obtained in samples using a CeO$_2$ buffer layer next to the YBCO.

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