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Non-magnetic Substrates for Low Cost YBCO Coated Conductors


Abstract—CuNiAl and NiCr alloys were made and processed to non-magnetic, bi-axially textured substrates. Epitaxial YSZ and YBCO were deposited by pulsed laser deposition on the CuNiAl. Samples were cross sectioned and investigated with TEM. It appears that Al forms a thin oxide layer at the CuNiAl surface that acts as a template for the subsequent YSZ layer. The 1.2 μm YBCO layer had a current density of 0.16MA/cm² at 75K and self field. On the NiCr substrates an Y2O3 seed layer was deposited with E-beam evaporation, followed by RF sputter deposition of YSZ and a CeO₂ cap layer. These substrates were coated with a 0.4 μm YBCO layer using a trifluoroacetate process, a very cost effective metal-organic solution process. These samples carried critical currents exceeding 0.7MA/cm² at 77K, self field.

Index Terms—YBaCuO Coated Conductor, Superconductor

I. INTRODUCTION

Development efforts for YBa₂Cu₃Oₓ Coated Conductors, or YBCO CCS, have greatly accelerated in recent years. The most obvious reason for this is the excellent self field and in-field performance of the conductor at 50-77K, in particular when compared with the now commercially produced Bi₂Sr₂Ca₂Cu₃Oₓ conductors. This makes the development of cost-effective deposition processes quite important. AMSC is therefore particularly interested in those processing steps where metal-organic deposition (MOD) processes based on cheap solutions can produce buffer or YBCO films with performance at par with similar films obtained through vacuum processing. For example, high Jc values have been obtained at AMSC using deformation textured substrates, vapor deposited epitaxial buffer layers, and a trifluoroacetate (TFA) based YBCO solution process. In 0.4μm thick films Jc reached 1.9 MA/cm² at 77K, SF [2], while 1μm thick films have been made with 1.0 MA/cm² with this TFA YBCO process [3]. High Jc values have also been obtained when the seed layer part of the buffer layer was deposited with a MOD process as well [3]. The substrates that were used were bi-axially textured Ni foils, with a Full Width Half Max (FWHM) value of 8-9°. Ni is considered a good demonstration metal, because it can be made well-textured with a surface that is compatible with epitaxial oxide deposition processes, whether these are physical vapor deposition processes or MOD processes such as have been used for the deposition of Gd₂O₃ seed layers. It has a tenacious bond with NiO, formed during YBCO processing, which reduces the chance of spallation at the Ni interface. However, Ni is ferro-magnetic which is problematic in many potential applications of YBCO CC. It is also quite weak when annealed to induce the cube texture. The use of strong, non-magnetic, oxidation resistant substrates with a sharp cube texture is therefore essential. The alloying of Ni to make it non-magnetic is relatively straightforward: in most cases the Curie decreases more or less linearly with increasing concentration of the alloying component, while the effect of the component is more or less proportional with its valence state. Cu (considered 1+) is the least effective element, but can alloy with Ni over the entire compositional range, and its low cost at high purity. Elements such as Al and Cr are three times more effective. Other elements such as W [9] and V [10] have been used as well. Here we report on the use of CuNiAl and NiCr alloys. The CuNiAl alloy has a small amount of Al to prevent
oxidation of the CuNi alloy which otherwise can oxidize nearly as fast as plain Cu. Note that small amounts of Al are quite effective, but that larger amounts can easily introduce a Ni(Cu)Al gamma prime component at 400-800°C. At temperatures below 900°C the external oxidation of an alloy such as CuNiAl was expected to form gamma alumina, which is cubic and has a lattice constant of 0.79 nm. The formation of this surface oxide was therefore expected to be compatible with the deposition of buffer layers such as CeO₂ or YSZ as the lattice match is quite good. Ni-13Cr is different, as the hexagonal Cr₂O₃ would most likely be a poor template for buffer deposition. In the NiCr case processing conditions were selected that would avoid premature oxidation of the substrate. ORNL has demonstrated on Ni-13Cr a Jₑ of 1.4 MA/cm² at 77K SF, using the e-beam BaF₂ process [8]. We were in particular interested to test the compatibility of NiCr with the solution-based trifluoroacetate YBCO process.

II. EXPERIMENTAL APPROACH
CuNiAl alloys with 48wt%Ni and 1-1.5% Al, and Ni with 13wt%Cr, were made by casting. The casts were deformed to tapes using a thermo-mechanical process. The CuNiAl substrates were 150 µm, the NiCr substrates 75 µm thick. The substrates were texture annealed using vacuum processing. The texture was analyzed using a Rigaku XRD system. In all cases the intensity of the (111) reflections in 0–2θ scans were well below 0.5% of the intensity of the (200) reflections. A Siemens (now Brucker-Axis) XRD unit with GADDS detector was used to make (111) and (200) pole figures. These were used to determine the percentages of the various substrate components: percentage with a cube texture, percentage of twins (these do not show up in 0–2θ scans) and percentage of grains with random or undesired texture. FWHM values were determined from the pole figures as well. The FWHM values are a statistical average over a relatively large area encompassing about 8-10,000 grains. The substrates were then prepared for buffer deposition. The CuNiAl was surface-cleaned to remove a thin alumina layer that forms during the texture anneal. For the PLD deposited buffer layers samples were polished to have a well-defined surface. The polished CuNiAl samples were coated with YSZ at LANL using PLD. The sample was heated in vacuum, held at elevated temperature for about 15 minutes, and coated with about 0.7 µm YSZ. Subsequently the substrate was coated with about 1.2 µm YBCO by PLD. The texture annealed NiCr substrates underwent a separate processing step to make their surface compatible with the buffer deposition process. A 20nm thick yttria seed layer was deposited by E-beam deposition. A 0.5 µm thick YSZ and 20nm ceria cap layer were deposited by RF sputtering. Buffer layers on the NiCr were inspected after seed layer deposition and after YSZ and ceria deposition with pole figures and HRSEM. The buffered NiCr sample was then coated with a 0.4 µm thick YBCO layer using the TFA YBCO solution process, similar as described before [2].

The critical current density was measured on bridged samples at 77K

Fig. 1 (111) pole figure of CuNiAl substrate, enhanced intensity

For the measurement of the thermal expansion some of the cast material was processed to rod. This approach is suitable as the thermal expansion in fcc metals does not depend on lattice direction, and the results from untextured rods are directly applicable to cube textured foils. For comparison a pure Ni rod was measured as well.

III. RESULTS
Fig. 1 and 2 show the pole figures of CuNiAl and NiCr, both at enhanced intensity (around 40-70x) to show background reflections. The CuNiAl has a slight tendency to form twins (the four reflections close to the center). These were observed with light microscopy to be short and relatively wide and located at grain boundaries, as is typical for annealing twins. Their percentage was 1-1.5%. The NiCr substrates were essentially free of twins. The FWHM values were 8-9° for the CuNiAl, and 7-8° for the NiCr. Fig. 3 shows the phi scan of the PLD deposited YBCO layer on YSZ/CuNiAl. The FWHM value is 17.8°. The YSZ has a lower FWHM of 13°. The 1.2 µm thick YBCO layer had a Jₑ of 160kA/cm² at 75K.
Fig. 2 (111) pole figure of NiCr substrate, enhanced intensity
Cross sectional TEM of a YSZ coated CuNiAl sample shows a thin, 20nm thick layer as can be seen in Figures 4 and 5. Chemical analysis of the layer identified it as alumina. Electron diffraction shows very weak reflections that appear to indicate gamma alumina, as shown in Fig. 5.

The CeO$_2$/YSZ/Y$_2$O$_3$/Ni-13Cr stack (E-beam yttria seed layer, sputtered YSZ and ceria cap layer) showed a much sharper texture for the buffer layer sequence. Fig. 6 shows the (111) pole figures of the ceria cap layer of this sample with FWHM values of 6-9°. Two samples that were coated with a 0.4 μm TFA YBCO layer both showed $J_c$ values exceeding 0.7MA/cm$^2$ at 77K, SF. No a-axis formation was evident from the XRD pattern, which was very clean as can be seen in Fig. 7.

The coefficient of thermal expansion (CTE) of CuNiAl was measured to be $13.8\times10^{-6}$/K at room temperature, while the cte of Ni was very close to that of NiCr, at $12.6\times10^{-6}$/K at RT. At higher temperatures the CTE for NiCr and Ni diverged somewhat.
Ni-13Cr samples showed the best texture of all, with a FWHM value of 6-9° being very close to that of the substrate. J results are lower than for corresponding Ni based samples, most likely due to a somewhat higher surface roughness of the alloy substrate.

### REFERENCES


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**Fig. 8** XRD scan for trifluoroacetate solution derived 0.4 μm thick YBCO layer on CeO$_2$/YSZ/γ-$\text{NiCr}$ substrate

Note that the CTE for Ni is slightly lower than generally quoted in the literature, which might be due to differences in purity, and the fact that some quoted CTE values are averaged over the 20-100°C temperature range.

### IV. DISCUSSION

The most obvious difference between the two substrates is the presence of a strong oxide former in CuNiAl. It is not clear when exactly the alumina layer formed before or after buffer deposition. Gamma alumina is hard to detect with XRD as it has a defect spinel structure, in which 21.3 Al atoms are randomly distributed over 16 octahedral and 8 tetrahedral sites. However, the post-deposition scenario does not seem likely as the cube-on-cube orientation of a YSZ layer on a clean, metallic CuNiAl surface would cause an unusual amount of lattice strain, much more than a 45° in-plane orientated YSZ layer would. The pre-deposition formation of a thin interface oxide such as cubic gamma alumina is comparable with the pulsed laser deposited YSZ on Ni, as was recently demonstrated by Lee et al. Here too a thin oxide layer, in this case (100) NiO, is expected to facilitate the cube-on-cube deposition. The reported J value of 0.5 MA/cm$^2$ at 77K, in a very thin PLD YBCO layer (250 nm) was considered high for a single buffer layer but lower than normal due to a certain degree of 45° mis-orientation of the YBCO film, as is also the case for the YBCO/YSZ/CuNiAl substrate in this work. The experiment with CuNiAl also demonstrated that substrates with coefficients of thermal expansion higher than that of Ni can still be a viable choice. In this case the difference is about 1.2x10$^4$/K, which will introduce an additional compressive strain on both buffer and YBCO layer of around 0.1%, assuming that the substrate does not yield.

The sputter deposited CeO$_2$/YSZ/CeO$_2$/CuNiAl yields a much better overall texture, with no deterioration of the texture with increasing buffer layer thickness. The buffered