Nickel-Copper Alloy Tapes as Textured Substrates for YBCO Coated Conductors

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Abstract. NiCuCo alloy tape was studied as textured substrates for YBCO coated conductors application. The addition of a small amount of cobalt was pursued in order to enhance the microstructure of the NiCu alloy. The use of different thermal treatments during the recrystallization process permitted to obtain area densities of cube orientation as high as 95%. The substrate was thoroughly characterized by means of x-ray diffraction, EBSD and SEM analyses. Further, the mechanical properties and the magnetic behaviour of this substrate have been investigated and compared with those exhibited by Ni, NiW and NiCu tapes. The suitability of this alloy substrate for YBCO coated conductors has been tested through the deposition of a conventional CeO$_2$/YSZ/CeO$_2$ buffer layer architecture using a Pd transient layer. Apart from passivating Ni-Cu-Co substrate, the use of a Pd transient layer produces a relevant texture sharpening in the out-of-plane orientation and the full width at half maximum of the $\omega$-scan drops from about 9° of NiCuCo to 2° of Pd layer. This sharp texture is transferred to the YBCO film and the results indicate that NiCuCo alloy is a promising alternative substrate for the realization of YBCO coated conductors.

1. Introduction

Ni-Cu alloys have been studied by several authors to obtain substrates with intermediate characteristics between Ni and Cu, since they form a continuous solid solution for all the relative concentrations [1-3]. In particular, high Cu concentrations have been studied, since Ni-Cu is non-magnetic at 77 K for Cu concentrations above 54 at.%. Ni-Cu alloys can be textured generally quite well, even though the cube tends to weaken at high concentrations. Besides, since the oxidation resistance of Cu-rich Ni-Cu alloys is as weak as pure Cu [4], some ternary alloys like Ni-Cu-Al and particularly Ni-Cu-Mn(Fe), namely constantan, have been recently studied. For the former, YBCO films were successfully grown and $J_c$ as high as 2 MA/cm$^2$, could be obtained only after sputtering the substrate surface to remove Al$_2$O$_3$ particles formed during recrystallization and using a novel TiN/MgO/LMO buffer layer architecture [4]. Constantan has been studied by several authors since it is a non-magnetic, commercially available alloy [3,5-7]. The low $J_c$ exhibited by YBCO film grown on such a substrate have been attributed to the surface roughness and/or oxidation phenomena [7].

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In the following, a detailed characterization of the ternary alloy NiCu\textsubscript{48.5}Co\textsubscript{3} (NiCuCo) substrate is presented and compared with Ni, NiCu\textsubscript{50} (NiCu) and NiW\textsubscript{5} (NiW) substrates. Further, its suitability as substrate for coated conductor application is shown through the deposition of a buffer layers architecture and YBCO films as well.

2. Experimental details

Ni, Cu and Co pieces, with nominal purities of 99.95+\% (Sigma-Aldrich), were melted in an argon-arc furnace with water-cooled copper hearth. First a Ni 50 at.\% Cu (NiCu) alloy was prepared. Part of this alloy was re-melted and an amount of 3 at.\% Co was added to form a ternary alloy (NiCuCo). In addition, Ni 5 at.\% W (NiW) alloy was produced. Further details on tape rolling are reported elsewhere [8]. Pd buffer layer was deposited by means of electron beam evaporation at temperatures ranging from 450 to 550 °C. The CeO\textsubscript{2}/YSZ/CeO\textsubscript{2} buffer layer architecture and the YBCO film were grown by pulsed laser deposition. Further details about buffer layer and YBCO film deposition are reported elsewhere [9].

Structural and morphological properties of the samples were analysed by means of X-ray diffraction, scanning electron (SEM) and atomic force microscopy (AFM). A Pseudovoigt fit was used for both ω- and ϕ-scans in order to evaluate the full width at half maximum (FWHM) of the distributions. The microstructure was investigated by means of electron backscattering diffraction (EBSD). The area of interest was sampled with a resulting pixel area of about 10 \(\mu\)m\textsuperscript{2}.

Hardness measurements have been performed using a Leitz–Wetzlar Vickers microhardness tester using a 200 g load. Stress-strain curves were measured at room temperature using an Instron 5500R testing machine with a 25 mm extensometer applied onto 100 mm long substrates prepared according to the ASTM E8M-99 test method for subsize specimen. The magnetic behaviour of the samples was studied by means of a vibrating sample magnetometer (VSM). Electric resistance measurements as a function of temperature \(R(T)\) of YBCO films were performed in a liquid nitrogen dewar by means of d.c. four-probe method. The critical current values were determined from the \(V-I\) characteristics with the standard 1 \(\mu\)V/cm electric field criterion.

3. Results and discussion

3.1 Texture development

The development of cube texture in the studied Ni-Cu alloys is dependent on the adopted recrystallization heat treatment. In fact, a conventional annealing at 900 °C for 4 hours leads to a cube area fraction as high as 93\% for NiCuCo and 51.1 \% for NiCu (figure 1).

![Figure 1](image.png)

**Figure 1.** Misorientation maps for NiCuCo (a) and NiCu (b) alloy tapes recrystallized for 4 hours at 900 °C.

Conversely, the two-step annealing (TSA), proposed by Sarma et. al. [10] and modified with a final plateau of 900 °C, leads to a remarkably smaller cube area fraction of 86\% for NiCuCo, whereas better
results are obtained with this method for NiCu, although the developed textures are still rather poor (see table 1). These results are likely due to the fact that the annealing parameters in the TSA method were optimized for NiW. Finally, a cube area fraction as high as 95% was obtained with NiCuCo when enhancing the temperature to 1000 °C, in agreement with what obtained by other authors [7,11-12]. From table 1 it can also be seen that substrates with larger cube areas exhibit at the same time a smaller area fraction of cube twins, in agreement with what previously reported [8,11].

Table 1. Area fraction of cube and cube twin (A_{cub}, A_{tw}), FWHM of ω-scan along both TD and RD (Δω_{TD}, Δω_{RD}) and FWHM of (111) ϕ-scan (Δφ) for Ni-Cu alloys subjected to different recrystallization treatments.

| alloy      | annealing | A_{cub} (%) | A_{tw} (%) | Δω_{TD} (deg.) | Δω_{RD} (deg.) | Δφ (deg.) |
|------------|-----------|-------------|------------|----------------|----------------|-----------|
| NiCuCo     | TSA       | 85.8        | 8.8        | 9.5            | 6.2            | -         |
| NiCuCo     | 900 ºC – 4h | 93.0        | 4.6        | 9.3            | 6.0            | 9.3       |
| NiCuCo     | 1000 ºC – 30’ | 95.0        | 4.0        | 9.1            | 5.9            | 9.2       |
| NiCu       | TSA       | 61.7        | 14.1       | 8.3            | 5.9            | -         |
| NiCu       | 900 ºC – 4h | 51.1        | 23.0       | -              | -              | -         |

In- and out-of-plane distributions of the (00l) orientation have been evaluated by means of (111) ϕ-scans and (002) ω-scans along both transverse (TD) and rolling directions (RD). All the distributions resulted to be almost Gaussian and the relative full width at half maxima (FWHMs) are reported in table 1. These data confirm that, for a given material, sharper textures are obtained for larger cube areas, in agreement with what previously reported for Ni-based alloys [8,11]. Hence, high temperature annealing is beneficial for the development of a strong, sharp cube texture, besides high temperatures favour the thermal etching phenomenon. Therefore, in the present work the recrystallization treatment has been limited to 1 hour at 900 ºC, which has been found to be sufficient to stabilize the microstructure of NiW substrates [12]. In the following, substrates annealed for 1 hour at 900 ºC will be referred to as recrystallized substrates.

The grain size for Ni-Cu alloy substrates annealed for 4 hours at 900 ºC is 26±5 μm for NiCuCo and 31±5 μm for NiCu, i.e. as in NiV or NiCr for the former and as NiW for the latter [13].

AFM measurements on recrystallized NiCuCo substrates provided grain boundary depth values for low- and high-angle boundaries of about 33 and 185 nm, respectively, i.e. very close to those reported for pure Ni substrates [14]. The intra-grain average and rms roughness are about 15.4 and 21.5 nm, respectively, i.e. larger than what reported for NiW rolled in the same conditions [8]. The measured roughness is the same if grain boundaries are included in the measured region.

Since the starting raw materials, as well as the whole thermo-mechanical process, remained the same for both Ni-Cu alloys, the enhanced cube texture development can reasonably be attributed to the addition of Co.

3.2 Mechanical properties

The addition of Co influenced the mechanical properties of the NiCu alloy, since the measured hardness on recrystallized substrates increased from 89 HV of NiCu to 103 HV of NiCuCo. This latter value indicate that the mechanical strength is comparable to that reported for Ni 2 at.% W alloy substrate [15].
The tensile properties of NiCuCo have been evaluated by means of stress-strain measurements and compared to those of NiW (figure 2). The yield strength ($YS$) measured at 0.2 % strain is 120 MPa, i.e. slightly higher than that exhibited by constantan alloy [5]. Though far from the tensile properties exhibited by NiW alloy, nevertheless the increased strength of NiCuCo alloy with respect to pure Ni tapes is relevant and indicate that this ternary alloy substrate could be successfully employed in a reel-to-reel deposition system.

3.3 Magnetic measurements

Figure 3a shows the mass magnetization as a function of the temperature $M(T)$ for the two Ni-Cu alloys. It is evident that the addition of Co has a remarkable effect on the magnetic properties of NiCu alloy. The Curie temperatures $T_C$ were extrapolated at $M=0$ using a fit curve $M \propto (T_C-T)^{1/3}$ [16] and $T_C=21.5$ and 157 K were found for NiCu and NiCuCo, respectively. The hysteresis loops $M(H)$ at 77 K for NiCu, NiCuCo and NiW recrystallized substrates are plotted in figure 3b. The hysteresis losses of NiCuCo are intermediate between those of NiCu and NiW. A detail in the low-field region reveals that the loop exhibited by NiCuCo is less skew with respect to that of NiCu (figure 3c). In fact, while in NiCu the magnetic domains are poorly correlated and for field below the coercition field some domains begin rotating, the presence of Co atoms contribute to couple the magnetic domains.

3.4 YBCO film deposition

Test samples of YBCO film deposited on the standard CeO$_2$/YSZ/CeO$_2$ buffer layer architecture were realized, either with or without the interposition of an additional Pd layer. The use of a Pd transient layer on the substrate revealed to be beneficial for both surface passivation and cube texture sharpening, and permitted the realization of coated conductors on challenging substrates such as NiCrW alloy [17] and to enhance the superconducting properties of YBCO films deposited on NiW [9]. In fact, in the case of Ni and NiW substrates a remarkable sharpening of the out-of-plane distribution of cube orientation was reported [18-19]. This behaviour was found also in Pd films.
deposited on both NiCu and NiCuCo alloy substrates, since the FWHM of the \( \omega \)-scan along TD drops from 9° of Ni-Cu to less than 2°.

Figure 4 shows the \( \theta \)-2\( \theta \) scan for YBCO/CeO\(_2\)/YSZ/CeO\(_2\) architecture grown on both bare and Pd-buffered NiCuCo substrate. In both cases films are well adherent, compact and without any crack. Both YBCO films are c-axis oriented and the only differences are the presence of broadened NiCuCo peaks caused by the diffusion of Pd into the substrate and the formation Cu oxide, revealed by a small CuO peak, in the sample without Pd.

The out-of-plane distribution of (00\( l \))YBCO is strongly influenced by the presence of the Pd transient layer. In fact, the FWHM of the \( \omega \)-scan of (005)YBCO dropped from 6.3° to 3.6° when a Pd layer is introduced. This latter value is however larger than that exhibited by the as-deposited Pd layer, indicating that an interdiffusion process occurred during the thermal ramp to 850 °C for CeO\(_2\) cap-layer and YBCO deposition, thus degrading the surface of the template.

Figure 4. \( \theta \)-2\( \theta \) scan for YBCO/CeO\(_2\)/YSZ/CeO\(_2\) films deposited on bare and Pd buffered NiCuCo tapes.

Figure 5. \( R(T) \) for YBCO/CeO\(_2\)/YSZ/CeO\(_2\) films deposited on bare and Pd buffered NiCuCo tapes.

Figure 6. \( J_c(B) \) at 77 K for YBCO/CeO\(_2\)/YSZ/CeO\(_2\) film deposited on Pd buffered NiCuCo.
Figure 5 shows the $R(T)$ of YBCO films deposited on both architectures. The critical temperatures $T_c$ values are 87.6 and 86.9 K for the sample with and without Pd, respectively. The measured critical current density $J_c$ for the sample with Pd is 0.31 MA/cm$^2$. Figure 6 shows the $J_c(B)$ for this sample. The rapid $J_c$ decrease in the low-field region is due to the grain boundaries, as previously shown [20]. These relatively poor properties of YBCO film are satisfactory taking into account that the YBCO coated conductors samples have been realized following the deposition process optimized for Ni-W tape.

**Conclusions**

A detailed characterization of the novel NiCu$_{48.5}$Co$_3$ alloy tape was presented and its suitability as textured substrate for YBCO coated conductors application has been tested. Though the obtained transport properties of YBCO film grown on this substrate are still limited and the substrate needs an improvement of the microstructure, the obtained results are encouraging and demonstrate the feasibility of YBCO coated conductors on Ni-Cu based substrates.

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