# Thermal treatments for biaxially textured Cu-Ni alloys for YBCO coated conductors

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J.L. Soubeyroux, C.E. Bruzek, A. Girard and J.L. Jorda

***Abstract*—We have studied the thermal treatments necessary to texture Cu-Ni alloys in view of applications as substrate for the YBCO coated conductors. Several alloy compositions chosen in order to avoid magnetism of the tapes have been elaborated by the rolling (RABiTS) method. Analyses of the texture as a function of annealing temperature have been done by X-ray and neutron diffractions, pole figures by EBSD and X-rays. The results show that the annealing temperature is dependant of the alloy composition and must be determined precisely for each composition. Good biaxial textures have been obtained on these cheap alloys.**

***Index Terms*—Cu-Ni substrate, superconducting tapes, YBCO coated conductor.**

## I. INTRODUCTION

THE rolling assisted biaxially textured substrates technique (RABiTS) is widely used for the texturation of nickel as substrates for HTS coated conductor production [1-6]. However for AC applications, hysteretic losses due to the ferromagnetism of Ni must be avoided. Then, several studies were carried out on non-magnetic materials. Solutions of Ni with metal such as W, Mo, V, Cr and Al [7-8] have given very good results, but the nickel is a relatively expensive material. Taking into account that copper is six times cheaper than nickel, and that copper and nickel form a full solid solution with the same cubic structure, the use of copper alloys is expected to give good results. In addition, alloys with less than 48% of nickel are non-magnetic below 77K [7]. Even pure copper alloys have been studied [9-10]. Today, copper-nickel alloys have been studied by Tuissi [11] on compositions with 10 and 30% of nickel. An unknown composition has also been studied by Yuan [12] and Shi [13]. Thieme and al. [14] and Cantoni and al. [10] have studied a ternary composition $Cu_{51}Ni_{48}Al_1$ where the role of aluminum is to produce, during further oxidation, a protective $Al_2O_3$ layer. De Boer et al. [7] have studied the compositions 33, 50 and 67% of nickel, but all the compositions have been recrystallized at 900°C and cube texture are much lower than the ones obtained with pure nickel or micro-alloyed nickel samples. In this study we present results obtained by RABiTS processing of copper-nickel alloys, recrystallized at various times and temperatures with textures comparable to the ones obtained on pure nickel.

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## II. EXPERIMENTAL

### A. Sample preparation

Three non-magnetic copper-nickel alloys were studied. In order to evaluate the possibility to use cheap industrial alloys, we used alloys of composition $Cu_{70}Ni_{30}$ and $Cu_{54}Ni_{45}Mn_1$ (Constantan®) from Goodfellow and an alloy $Cu_{90}Ni_{10}$ from Clal-MSX. The analysis of the main impurities of the three studied alloys is reported in table 1.

TABLE I
ANALYSIS OF THE MAIN IMPURITIES IN THE STUDIED ALLOYS

| Alloy | Fe (ppm) | Ca (ppm) | Mg (ppm) | Si (ppm) | Mn (ppm) |
|---|---|---|---|---|---|
| $Cu_{54}Ni_{45}Mn_1$ | 2500 | | | | 7500 |
| $Cu_{70}Ni_{30}$ | 11120 | 217 | 57 | | |
| $Cu_{90}Ni_{10}$ | 700 | 214 | 56 | 129 | |

The alloys were delivered as cylinders with respective diameters 8, 12.7 and 4 mm for $Cu_{54}Ni_{45}Mn_1$, $Cu_{70}Ni_{30}$ and $Cu_{90}Ni_{10}$ respectively. Cold rolling was realized on two different Redex rolling mill and the final thickness were 150, 110 and 100 µm, corresponding to deformation rates of 98.4, 99.1 and 97.0% for $Cu_{54}Ni_{45}Mn_1$, $Cu_{70}Ni_{30}$ and $Cu_{90}Ni_{10}$ alloys respectively.

### B. Characterizations

X-ray pole figures were performed on a Siefert goniometer mounted on a standard RX generator using a copper tube ($K_{\alpha 1}$, $K_{\alpha 2}$).

Neutron diffraction experiments were performed on the D1B diffractometer of ILL-Grenoble which is equipped with a 400 cells position sensitive detector, covering an 80° 2-theta range, and allowing recording a pattern every 5 minutes. The experiments were performed in a dedicated furnace with a vanadium resistor under a secondary vacuum. The wavelength used was 0.2524 nm.

The electron back scattering diffraction (EBSD) measurements were performed using a JEOL 840A SEM at 20kV, at a working distance of about 22 mm and a specimen tilt of 70°. Pictures were imaged on a phosphor screen, viewed by a HAMAMATSU camera and the ARGUS image processor. Channel 5 HKL software was used to index the grains' orientation. A final picture of 400*400 µm² with a measurement step of 4 µm was obtained.

## III. Results and discussion

After cold rolling, the samples were cut in pieces of 2 cm by 1 cm. An X-ray diffraction experiment in Θ-2Θ scan was performed on each sample. These scans show that there is some orientation of the cubic structure in the 002 direction, we have extracted the cubic cell parameters from these data and plotted the a cell parameter as a function of copper-nickel composition in figure 1. This plot shows that the alloys fulfill the Vegard's law of metals with the same crystal structure.

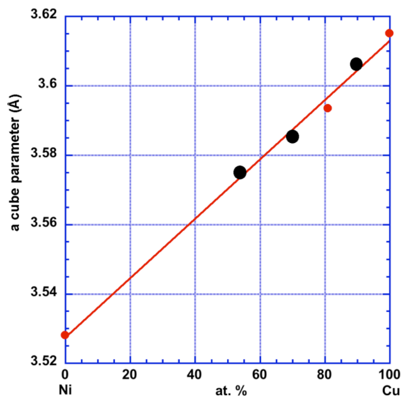


Fig. 1. Cubic cell parameter of the different alloys, bigger circles are studied samples, the other data are extracted from ICSD powder data files.

Different thermal treatments were applied in a first time under secondary vacuum, by heating at various temperature the sample and applying a plateau temperature of 120 min at each temperature. At the end of these thermal treatments, X-ray diffraction Θ-2Θ scans were performed and plotted in figures 2, 3 and 4 for the respectively $Cu_{54}Ni_{45}Mn_1$, $Cu_{70}Ni_{30}$ and $Cu_{90}Ni_{10}$ alloys.

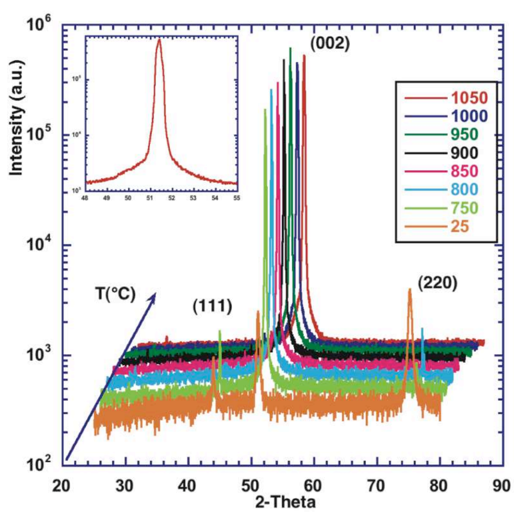


Fig. 2. X-ray Θ-2Θ scan performed on the $Cu_{54}Ni_{45}Mn_1$ alloy after the heating treatments reported in text. Scans are presented with increasing temperature.

For the $Cu_{54}Ni_{45}Mn_1$ alloy, at 750 and 800°C, the (111) and (220) lines are still present; between 850 and 950°C, we observe only the (200) line with a regular lorentzian shape; at 1000°C and 1050°C there is an enlargement of the basal peak shape (see insert of fig. 2) probing an increase of defects. The sample annealed at 950°C has been chosen for the characterization of texture.

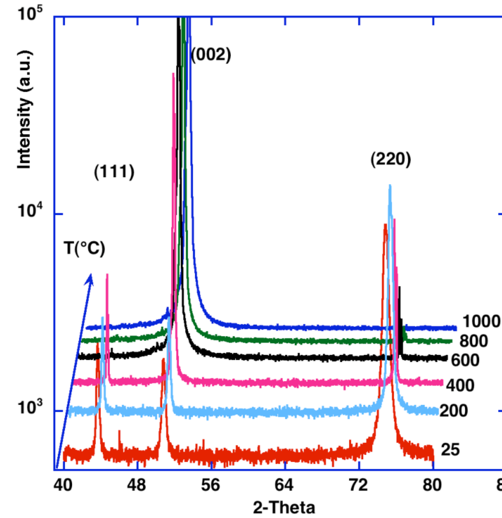


Fig. 3. X-ray Θ-2Θ scan performed on the $Cu_{70}Ni_{30}$ alloy after the heating treatments reported in text.

For the $Cu_{70}Ni_{30}$ alloy, up to 600°C, the (111) and (220) lines are still present, but at 800°C, only the (002) line is present with a sharp line profile. The diagram recorded at 1000°C shows only the (002) line, but with an enlargement of the foot of the peak. So the adequate temperature for annealing this sample ranges between 800 and 1000°C, but we need more experimental results to determine precisely this temperature.

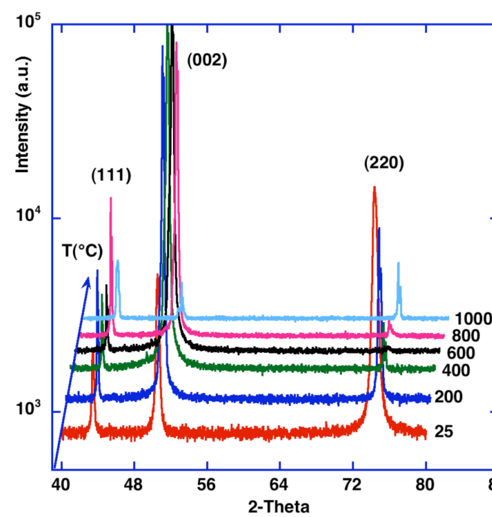


Fig. 4. X-ray Θ-2Θ scan performed on the $Cu_{90}Ni_{10}$ alloy after the heating treatments reported in text.

For the $Cu_{90}Ni_{10}$ alloy, up to 400°C, the (111) and (220) lines are still present; at 600 and 800°C, the (002) line is present with a sharp line and a small contribution of the (220), but the (111) line is present for these two temperatures. At 1000°C, the cube texture disappears and the (111) is the most intense line of the diagram. So the adequate temperature for annealing this sample ranges between 600 and 800°C, but we need more experimental results to determine precisely this temperature as for the previous sample.

Powder neutron diffraction studies have been performed on laminated samples. Pieces of 5 cm long and 0.4 cm wide have been placed parallel in a vanadium container with the laminated face parallel to an axis aligned at 37.5° from the incident beam. The detector was set at a fixed 2Θ angle between 50 and 130°. In this geometry, when the sample becomes orientated with a cube texture perpendicular to the rolling plane, the (002) line diffracts in the detector with a maximum of intensity. The experiments performed at a heating rate of 2°/min, with a diagram recorded every 5 min are reported in figures 5 and 6 for the alloys $Cu_{70}Ni_{30}$ and $Cu_{90}Ni_{10}$ respectively.

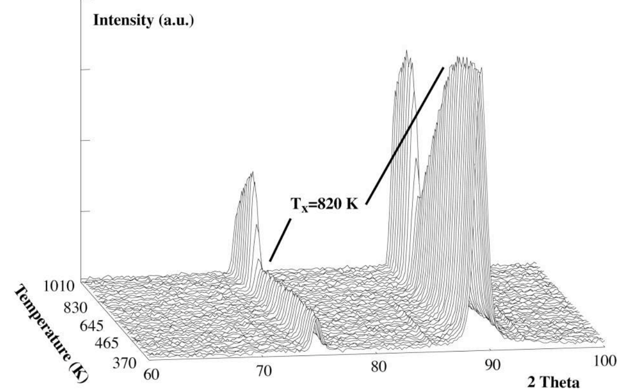


Fig.5. Neutron diffraction 3D-plot performed on the $Cu_{70}Ni_{30}$ alloy.

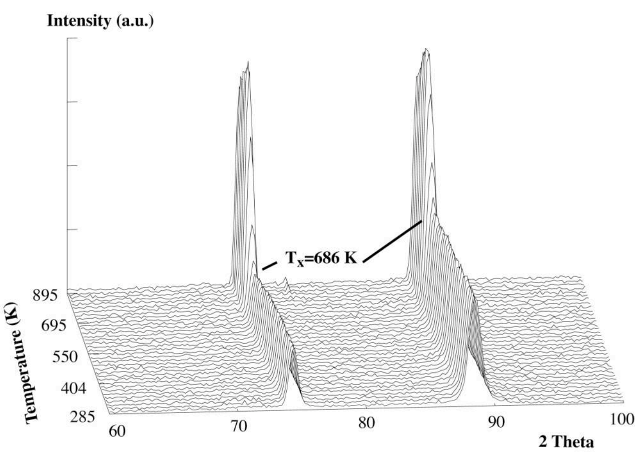


Fig.6. Neutron diffraction 3D-plot performed on the $Cu_{90}Ni_{10}$ alloy.

The experiment shows that the $Cu_{70}Ni_{30}$ alloys starts to be reoriented at 820K (547°C), which is consistent with the experiments made on ex-situ samples with X-ray, but due to the dilatation of the cell parameter, the angle of diffraction of the (002) line (Θ angle) was no more in the diffraction plane, and it was impossible to get more results at higher temperature. The same experiment performed on the $Cu_{90}Ni_{10}$ alloy shows a beginning of reorientation at 686K (413°C), which is also consistent with lower reorientation, and recrystallization temperatures observed on ex-situ X-ray experiments.

The textures of the tapes were characterized by means of the SEM-based EBSD technique. An EBSD orientation map, pole figure and histograms of a $Cu_{54}Ni_{45}Mn_1$ alloy, annealed at 950°C for 5 min under argon atmosphere, is shown in figure 7.

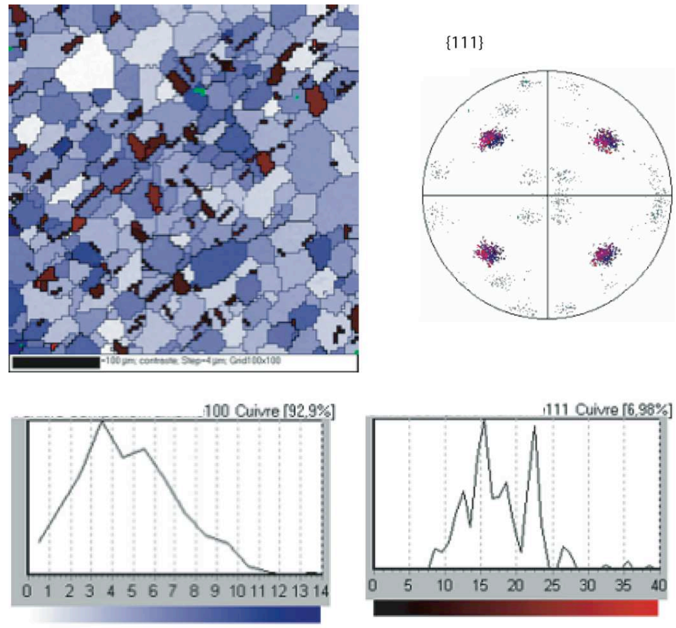


Fig.7. EBSD orientation map, pole figure and histograms of the $Cu_{54}Ni_{45}Mn_1$ alloy, annealed at 950°C for 5 min under argon atmosphere.

It may be seen that 93% of the grains have the good cube texture with a deviation angle from the [200] direction of 4°, the disoriented grains (7%) are mainly in the [111] direction with a deviation angle from this direction of 15°.

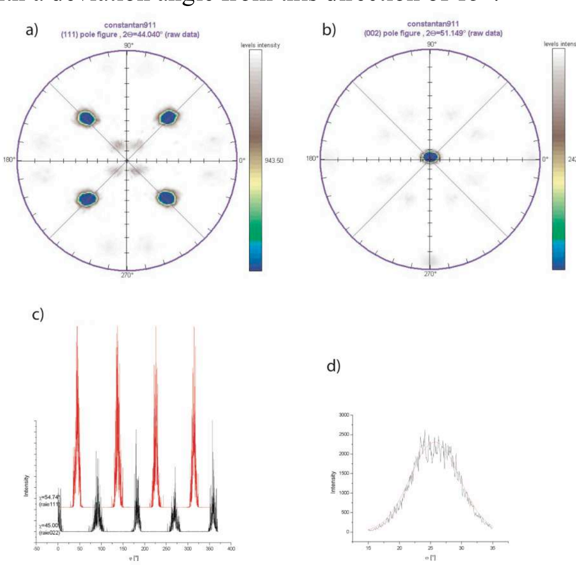


Fig.8. X-ray pole figures of the $Cu_{54}Ni_{45}Mn_1$ alloy, annealed at 950°C for 5 min under argon atmosphere. a){111}, b) {002}, c) (111) and (022) ω scans d) (002) φ scan.

The figure 8 shows the X-ray diffraction pole figures, ω and ϕ scans performed on the (111) and (022) lines, on a constantan sample annealed at 950°C for 5 min. under argon atmosphere. The ω scan presents a full width at half maximum (FWHM) of the peak of 7.3°. The ϕ scans present FWHM of 7.2 and 8.6° for the (111) and (022) lines.

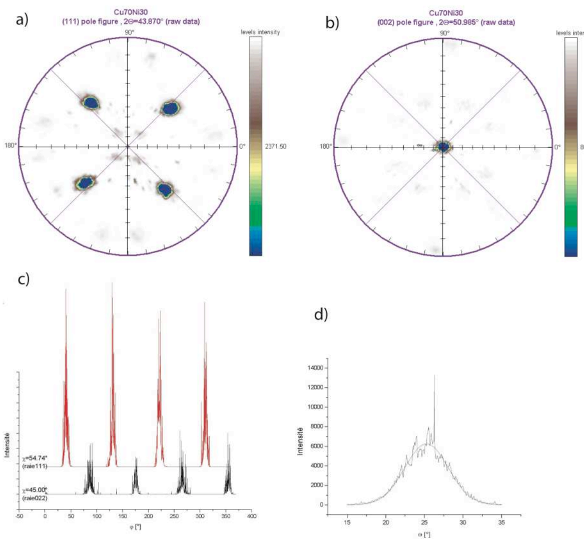


Fig.9. X-ray pole figures of the $Cu_{70}Ni_{30}$ alloy, annealed at 900°C for 720 min under argon atmosphere. a){111}, b) {002}, c) (111) and (022) ω scans d) (002) φ scan.

The figure 9 shows the X-ray pole figures, ω and ϕ scans performed on the 111 and 022 lines, on a $Cu_{70}Ni_{30}$ alloy annealed at 900°C for 720 min. under argon. The ω scan presents FWHM of 5.7°. The ϕ scans present FWHM of 5.8 and 7.2° for the (111) and (022) lines. A sample annealed at 900°C for 5 min. gives FWHM values of 6.9°, 6.9° and 7.8° for the same respective scans.

## IV. Conclusion

Three Cu-Ni alloys have been studied for application as cheap substrates for YBCO coated conductors. The recrystallization temperatures have been estimated from X-ray experiments, the temperature ranges determined are decreasing from Ni-rich to Cu-rich alloys. In the process that we have chosen for the YBCO deposit, the substrate will be heated for some time at 850°C, so during this processing step the alloy must be stable. So we have eliminated in further annealing studies the $Cu_{90}Ni_{10}$ alloy that is not stable at this temperature. For pure copper alloys, annealing temperatures have been found to be efficient at 600°C, but annealings performed above 800°C have modified the cube texture. This confirms that thermal stability of the cube texture for Cu-Ni alloys decreases for Cu-rich alloys. We have also demonstrated by in-situ neutron diffraction that the beginning of the recrystallization was varying with composition and decreasing also for Cu-rich alloys. A constantan sample annealed at 950°C for 5 minutes presents very good cube texture, with FWHM of 7.3° for the 002 line. The $Cu_{70}Ni_{30}$ alloy annealed at 900°C for 5 minutes presents a very good cube texture, with FWHM of 6.9° for the 002 line. Improvement of the texture of this alloy has been done by a long annealing time of 720 minutes. The resulting texture presents a FWHM of 5.7° for the 002 line, 5.8° for the 111 line and 7.2° for the 022 line with a very high percentage of the grains in the adequate {002} orientation. Further EBSD experiments will be done on this sample. It has been demonstrated that these substrates are suitable for further layer oxide deposition at 850°C, as their cube texture increases with annealing time.

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