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Industrial Cu-Ni alloys for HTS coated conductor tape.

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Abstract. Copper rich Cu-Ni alloys have been textured with the RABiTS method in order to get non-magnetic and cost efficient substrates for coated conductor wires. The study is focused on two industrial compositions: $Cu_{55}Ni_{45}$ (Constantan) and $Cu_{70}Ni_{30}$. Studies on surface roughness have been done. The effects of annealing conditions (temperature and atmosphere) on the grain boundaries deepness were analyzed. Electrolytic polishing was also applied to improve the surface quality. RX pole figures and micro hardness measurements have been achieved on samples annealed up to 950°C. Attention has been paid to the rolling texture and to the annealing processes. The rolling texture has been found to be mainly copper-type (C, S and B contributions). Beginning of recrystallization occurred between 400°C and 600°C and stabilized between 900°C to 950°C, depending on the nickel content of the alloy. Finally both samples, rolled and annealed under the appropriate conditions, have been characterized. Pole figure measurements gave the global in plane and out of plane disorientations of our samples which are in-plane 7.4° and out-plane (RD) 4.3° for both samples. EBSD maps have shown the details of the distribution and have allowed us to quantify the ratio between cubic {100}<001> and twined {122}<21-2> orientations.

1. Introduction

Manufacturing a bi-textured substrate is one of the critical steps for the HTS coated conductor development. The RABiTS (Rolling Assisted Biaxially Textured Substrate) method is widely used [1] with nickel as base material due to its good texture properties and its cell parameter which conveniently fits the YBCO (a,b) plane.

However, for AC applications, the magnetism of pure nickel generating hysteretic loses could decreases the performance of the wire. The addition of some metallic impurities (Mo, Cr, W and Cu for instance), allows to shift the Curie temperature down to 77 K. Among these alloying metals, the copper is one of the most interesting: the nickel-copper system is a lens system with complete, nearly ideal solutions in liquid and solid states. Single phase alloys with more than 53 at.% Cu would then combine the good texture properties of Ni with the non-magnetic property of copper. Economic aspect is also to be considered, as the copper is five times cheaper than nickel. Substrates with copper content from 50 to 90 at.% already have been prepared [2,3]. We present here studies on the surface state and the texture ability relation of the industrial Constantan® ($Cu_{55}Ni_{44}$) alloys tapes. Result will be compared with the $Cu_{70}Ni_{30}$ alloys tape.

2. Preparation and characterisations

2.1. Sample preparation

The two non-magnetic copper-nickel alloys studied, with composition $Cu_{55}Ni_{45}$ and $Cu_{70}Ni_{30}$ from Goodfellow, were delivered as cylinders with respective diameters 8 and 12.7 mm. Cold rolling was realized on a Redex rolling mill with two CW roll with mirror aspect. Rolls diameter is 64 mm and rolling speed is about 1-3 m/min. Final deformation of the tape is about 98-99 % with 8 % deformation each pass. Annealing treatments were adjusted (see previous work [4]), to 950°C and 900°C for constantan and $Cu_{70}Ni_{30}$, respectively.

Special attention was given to the surface aspect of the tapes which were always handled with powder-free gloves. The rolls were cleaned after each pass.

2.2. Characterisation

Roughness aspects were mainly studied with an Autoprobe CP research AFM, used in contact mode. X-ray pole figures were performed on a Siefert goniometer mounted on a standard RX generator using the copper (Kα1, Kα2) radiations.

Electron back scattering diffraction (EBSD) measurements were performed using a JEOL 840A SEM with an accelerating voltage of 20 kV, at a working distance of about 22 mm and a specimen tilt of 70°. 400*400 μm^2 pictures were displayed on a phosphor screen, recorded by a HAMAMATSU camera.

3. Results and discussions

3.1. Surface aspect

The tapes obtained with mirror polish rolls do not need any further polishing step. The studies were focussed on the formation of grain boundary (GB) gaps during annealing which cause the main part of the roughness.

Initially, the thermal treatment consisted of a two hours plateau at 950°C, under vacuum in presence of Ti sponge to avoid oxidation. Figure 1a shows the deep boundary (500 nm) which is formed between the grains after this treatment. We assumed that this behavior was due to the evaporation of the copper or some others impurities. Then the thermal conditions were changed. Figure 1b shows GB on a tape heated without plateau keeping unchanged the vacuum condition, whereas in figure 1c the sample was isothermally (950°C) annealed for 2-hours in argon atmosphere (1 bar). In both cases, obviously, the GB have been reduced (around 100 nm). They completely disappeared by combining the two effects: no temperature plateau and one bar of argon (figure 1d).

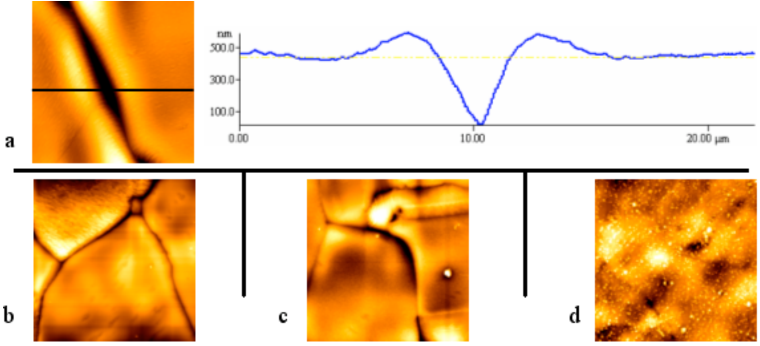

Figure 1. AFM mapping (20*20 μm^2) of Constantan rolled and annealed at 950°C, a) 2h in vacuum (with associated cross section), b) 0h in vacuum , c) 2h in argon (1 bar); d) 0h in argon.

So, a short annealing time at high temperature in presence of a neutral gas at a pressure of about 1 bar are the conditions which avoid copper evaporation and consequently, which yield to a smooth surface state. It is noteworthy that in some cases electro-polishing has been successfully performed in order to improve this surface state.

3.2. Texture aspect

The surface pole figures of rolling tapes have been investigated. Results for Constantan (figure 2), showed that the maximum intensity agreed with the B, S, C components whereas the Goss component (triangles), typical to the brass type deformation, is not present. We can conclude to a “copper” type deformation texture of our Cu-Ni alloy.

After a heavy mechanical polishing step, similarly pole figures have been found in the heart of the tape. This, indicating that no shear deformation (100){011} appear on the surface, with our rolling conditions.

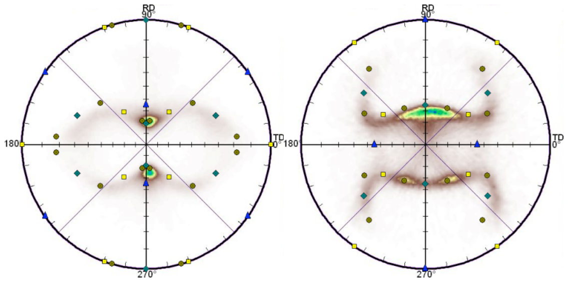

Figure 2. (111) and (200) pole figures (linear scale) of Constantan after rolling with theoretical C◆, S●, B□ and G▲ components.

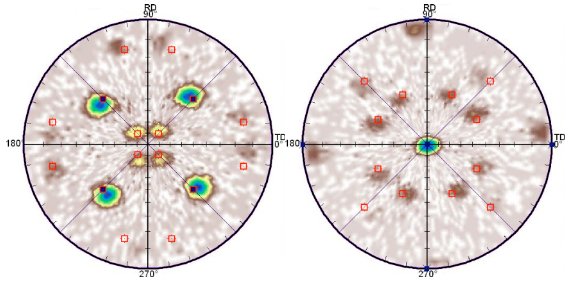

Figure 3. (111) and (200) pole figures (logarithmic scale) of Constantan after annealing at 950°C with theoretical cubic✖ and twin□ components.

Study of annealed texture with pole figures measurements is presented figure 3. The cubic (100){001} texture is predominant but a small twin component (122){21-2} still remains (empty squares).

The cubic texture is characterised in terms of in-plane and out-plane texture in figures 4 and 5. The in-plane texture given by the FHWM average of the four peaks of the 111 ϕ-scan is around 7.8°. The out of plane texture in the rolling direction is 4.3° which is smaller than that in the transverse direction: 7.0°.

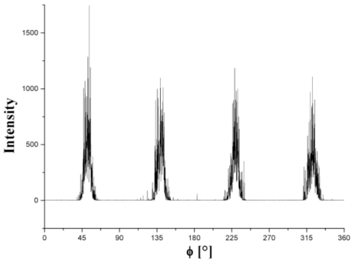

Figure 4. 111 ϕ-scan on a Constantan annealed sample.

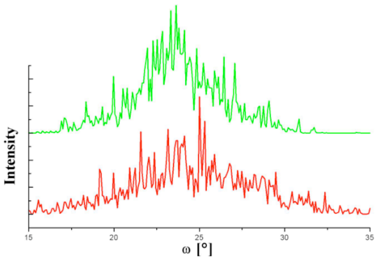

Figure 5. ω-scan (rocking curve) on the rolling (up) and transverse (down) directions on a Constantan annealed sample.

EBSD maps of the annealed constantan tape were measured (figure 6) to quantify the proportion of the twinned grains and to observe the separation line on the surface of grains with different orientations.

The average diameter of cubic oriented grains is 50 μm; they are randomly distributed around the (200) direction. Black grains, roughly distributed around the (122) direction correspond to the twin orientation of the copper cubic structure. They are mostly elongated in the (100){011} direction and represent 7 % of the surface. This kind of grain is probably due to the smaller stacking fault energy of the alloy compared to pure nickel.

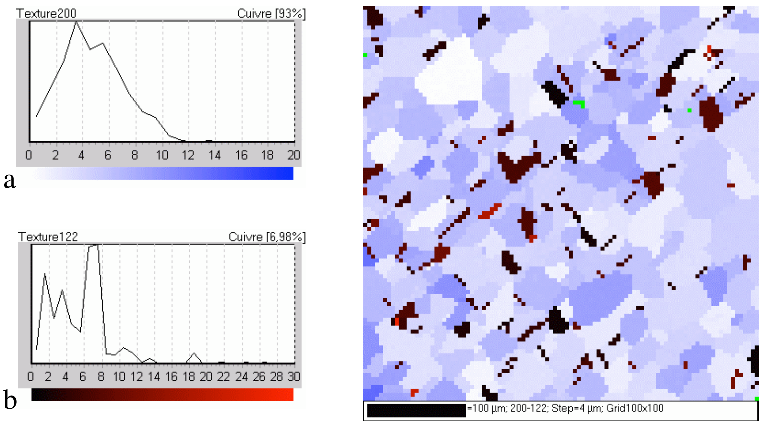

Figure 6. EBSB map of Constantan annealed at 950°C. a) cubic texture distribution around the (200) axis; b) twin texture distribution around the (122) axis.

Similar results have been found in terms of twin content and in-plane, out-plane disorientations for the $Cu_{70}Ni_{30}$ tape.

4. Conclusion

The relations between the surface state and the ability to form a bi-axially textured tape for HTSC applications have been studied for the industrial alloys, Constantan and $Cu_{70}Ni_{30}$. It was found that the initial surface roughness of the annealed tapes, mainly due to the grain boundary gaps, may be drastically reduced with appropriated annealing conditions, in particular in applying no high temperature isothermal plateau under neutral gas atmosphere (Argon).

A typical pure metal deformation texture has been found for as-rolled tapes, which yielded, after annealing, to a very good cube texture: in-plane 7.8° and out-plane 4.3° (rolling direction). The (122){21-2} direction, which represents 7 % of the surface, corresponds to twin formation.

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