Highly cube textured Cu-based substrates for YBCO-coated conductors

R Nast¹, B Obst¹, W Goldacker¹ and B Holzapfel²
¹Forschungszentrum Karlsruhe, Institut für Technische Physik, Postfach 3640, D-76021 Karlsruhe, Germany
²IFW Dresden, Helmholtzstraße 20, D-01069 Dresden, Germany
E-mail: rainer.nast@itp.fzk.de

Abstract. Cube textured Cu/Cu-based tapes are shown to be an alternative to Ni/Ni alloy substrates widely used in high current capability YBCO-coated conductors. Copper, other than nickel, is non-magnetic and has a larger thermal and electrical conductivity, keeping up thermal stabilization of the superconductor at cryogenic temperatures. Jointly with the cube texture of exceptional strength that develops after rolling and recrystallization, Cu is, therefore, a candidate material for coated conductor architecture.

In this work, we report on the texturing of pure copper and different copper alloys, such as Cu-Mn and a dispersion hardened Cu-B₄C tape. For Cu and Cu-B₄C, the maximum found in the cube texture histograms are 3.8° and 4.4°, respectively.

1. Introduction
Much progress has been made in the development of second-generation HTS tapes over the past years. In the so-called RABiTS™ (rolling assisted biaxially textured substrates) technique [1] a cube textured metal based substrates is epitaxially coated with oxide buffer layers and YBCO. As metallic templates for these coated conductors one mainly focused on cube textured Ni or Ni alloys, such as Ni-W, Ni-Cr, Ni-V, Ni-Cu or Monel [2-6]. Because of their relevance for technical properties, the rolling and annealing textures of f.c.c. metals and alloys have been studied over decades in great detail, and the rules for cube texture formation are well established [7-10].

An alternative f.c.c. material to Ni/Ni alloys which can be easily textured is copper. Potential advantages over Ni are the non ferromagnetism, minimizing hysteretic losses in ac-applications, a five times lower resistivity and an about 20% higher heat capacity. So, Cu substrates can offer thermal and electrical stability if a conductive buffer can be successfully applied. Furthermore copper is less expensive (up to six times). Therefore, great efforts are made to develop Cu-based tapes for coated conductors [11-13]. The present work will focus on the texturing of pure copper, Cu₉₈Mn₂ and Cu-0.4 vol% B₄C.

2. Experimental
As-received electrolytic copper (E-Cu 99.9 wt.%) rods of 24 mm diameter were first annealed at 400°C for 2 h in an Ar-5 vol% H₂ gas mixture and then swaged down to 7.5 mm with one intermediate annealing and a final treatment at again 400°C / 2 h.
The Cu-0.4 vol% B₄C was prepared using a powder metallurgical approach. 99.9 wt% Cu powder of about 60-220 µm and 99.4 wt% B₄C powder of about 1-7 µm from Alfa Aesar were mixed together. The pre-compressed powder was then cold isostatically pressed with 500 MPa and sintered at 950°C / 6h in vacuum (1x10⁻⁵ mbar). The sintered compact of about 12.4 mm diameter with a porosity of 10% was swaged down to 7.5 mm and annealed at 500°C / 2h in Ar-5 vol% H₂.

The Cu₉₈Mn₂ alloy was inductively melted, homogenized at 1000°C / 5 h in Ar-5 vol% H₂, lathe off to 25 mm and swaged down to 14.5 mm. After an annealing at 500°C / 2 h in Ar-5 vol% H₂ the rod was further swaged to 7.5 mm and annealed again at 500°C / 2 h.

All rods were then heavily cold rolled with an aspect ratio of \( l/d_0 \) > 1 per pass \( (l_0 \) projected contact length to the rolls, \( d_0 \) specimen thickness) to obtain a homogeneous deformation [14]. The relative thickness reduction was 98.7%. The cube texture was formed during recrystallization at temperatures between 400 and 900°C for 30 min in an Ar-5 vol% H₂ gas mixture or in vacuum (4x10⁻⁶ mbar).

After recrystallization and grain growth the E-Cu tapes were electrotyically plated with Ni. We used a Watt’s bath (240 g/l NiSO₄·7H₂O, 30 g/l NiCl₂·6H₂O, 20 g/l H₃BO₃) at 50°C / 2 A dm⁻² [15].

The textures of the tapes and platings were characterized by means of the SEM-based EBSD technique (HKL Technology); for details see [16].

3. Results and Discussion

As reported in [17] the Cu tapes show individual cube-oriented elongated grains after cold rolling, lined up along the rolling direction (RD). The size of the grains grows with time at ambient temperature.

![EBSD orientation map, pole figure, and histograms of E-Cu, recrystallized at 900°C for 30 min in Ar-5 vol% H₂.](image)

Annealing at 900°C / 30 min in Ar-5vol% H₂ produces an exceptional sharp cube texture with a maximum in the cube texture histogram at 3.8° and a \{111\} pole density maximum of about 115 x random (Ni-W max. 85 x random; the contour levels have been calculated with 5°, both for Gaussian
half width and cluster size). Figure 1 shows the EBSD orientation map, pole figure and histograms of this highly cube textured tape. The microstructure exhibits a pronounced grain elongation in rolling direction with aspect ratios up to 4:1, causing rather large effective grain boundary areas for current flow. This microstructure is supposed to enable a significant enhancement of critical currents in coated conductors [18]. To confirm this suggestion, a simulation of the current carrying capability with the limiting path model was performed, using the EBSD texture data of the E-Cu substrate, assuming the epitaxial growth of buffer layers and YBCO (for a detailed model description see [19]). The simulation resulted in 78% of the $J_c$ value which was found for single low angle grain boundaries at 77 K. So far, this is a value never reached before.

With an increasing amount of alloying elements in Cu alloys (decreasing stacking fault energy SFE) the rolling texture changes from the Cu-type into the brass-type rolling texture. This essentially results in the recrystallization texture of brass $\{236\}<385>$ as well as in a great variety of apparently complex transition textures [7-9]. Manganese is the only alloying element that does not alter the SFE of copper alloys. In figure 2 the EBSD orientation map, pole figure and histograms of Cu$_{98}$Mn$_2$ are shown. Despite the unchanged SFE the cube texture in Cu$_{98}$Mn$_2$ is less pronounced and additional texture components appear like the rotated cube $\{013\}<100>$ (rotation about the rolling direction), twins $\{122\}<212>$ and the R texture $\{124\}<211>$ (figure 2). This is in good agreement with literature data [20]. Changes in the as-deformed microstructure cause mainly these texture changes. In particular shear bands forms with both deformation degree and Mn content, providing additional nucleation sites for other orientations, see [20]. So, Cu$_{98}$Mn$_2$ is far away from the use as substrate in coated conductors.

![Figure 2. EBSD orientation map, pole figure, and histograms of Cu$_{98}$Mn$_2$, recrystallized at 750°C for 30 min in vacuum (4x10$^{-6}$ mbar).](image)

Dispersion hardening is another reasonable kind of hardening soft metals. In the case of copper dispersed particles usually lead to a reduction of the cube texture while maintaining the rolling texture and/or promote a preferential growth of other orientations. Nevertheless, for certain volume fractions...
and grain sizes of B₄C the sharp cube texture of Cu remains unchanged to a large extent [21]. The Cu-0.4 vol% B₄C tape shown in figure 3 point out the achieved sharp cube texture with a maximum in the cube texture EBSD histogram at 4.4°. But there is no grain structure visible in the EBSD orientation map. This is caused by the relatively high porosity of 10% which make some problems during rolling and annealing of this material. However, Cu-0.4 vol% B₄C tapes are a good dispersion hardened alternative to pure copper tapes for coated conductors.

Copper other than Ni is much more susceptible to surface oxidation during buffer layer deposition. To overcome this problem the Cu tapes could be protected by the deposition of a more oxygen resistant metal layer. Beside noble metals an alternative overlayer is Ni. For the deposition of Ni we used electroplating described in detail in [22]. As described in [17, 22] the Ni layer grow epitaxial on the substrate. In contrast to [22] we used a Watt’s bath for plating. With this electrolyte the as-deposited Ni film already shows the epitaxial developed cube texture without any additional annealing.

Figure 3. EBSD orientation map, pole figure, and cube texture histogram of Cu-0.4 vol% B₄C, recrystallized at 400°C for 30 min in Ar-5 vol% H₂.

4. Summary
We investigated the texturing of cold rolled and recrystallized Cu and Cu alloys like E-Cu, Cu₉₂Mn₂ and Cu-0.4 vol% B₄C. In E-Cu the microstructure of the as-rolled specimen shows elongated cube textured grains depending on time of storage (partial recrystallization at room temperature). After annealing at 900°C for 30 min an intensely sharp {001}<100> cube texture with a maximum in the cube texture EBSD histogram at 3.8° results. The microstructure exhibits a pronounced grain elongation in rolling direction with aspect ratios of 4:1. Simulation of the Jₑ at the IFW Dresden resulted in a value of 78% of the value for single low angle grain boundaries at 77 K which was never reached before.
Compared to E-Cu the cube texture in Cu$_{98}$Mn$_2$ is weakened and additional texture components appear like the rotated cube {013}<100> (rotation about the rolling direction), twins {122}<212> and the R texture {124}<211>.

A surprisingly sharp cube texture was achieved in Cu-0.4 vol% B$_4$C. The maximum in the cube texture histogram at 4.4° and a {111} pole density maximum of 88 x random are in the range of the best Ni-W tapes. Because of the relatively high porosity of 10% no grain structure is visible in the EBSD map. With an optimization of the powder metallurgy process Cu-0.4 vol% B$_4$C tapes could be a good dispersion hardened alternative to pure copper tapes for coated conductors.

Electroplating of Ni on E-Cu prevents the surface oxidation of copper during buffer layer deposition. The cube texture in the Ni film develops epitaxially on the substrate without any post annealing. This non-vacuum process is suitable for a low cost, economical and easily scalable long lengths production of coated conductors.

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