On the use of copper-based substrates for YBCO coated conductors

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Abstract. It is well known that the recrystallization texture of heavily cold-rolled pure copper is almost completely cubic. However, one of the main drawbacks concerning the use of pure copper cube-textured substrates for YBCO coated conductor is the reduced secondary recrystallization temperature. The onset of secondary recrystallization (i.e., the occurrence of abnormal grains with unpredictable orientation) in pure copper substrate was observed within the typical temperature range required for buffer layer and YBCO processing (600–850 °C). To avoid the formation of abnormal grains the effect of both grain size adjustment (GSA) and recrystallization annealing was analyzed. The combined use of a small initial grain size and a recrystallization two-step annealing (TSA) drastically reduced the presence of abnormal grains in pure copper tapes.

Another way to overcome the limitation imposed by the formation of abnormal grains is to deposit a buffer layer at temperatures where secondary recrystallization does not occur. For example, La₂Zr₂O₇ (LZO) film with a high degree of epitaxy was grown by metal-organic decomposition (MOD) at 1000 °C on pure copper substrate. In several samples the substrate underwent secondary recrystallization. Our experiments indicate that the motion of grain boundaries occurring during secondary recrystallization process does not affect the quality of LZO film.

1. Introduction

The use of pure copper biaxially textured substrate for YBa₂Cu₃O₇₋δ (YBCO) coated conductor was studied by some authors during the last ten years [1–3]. In fact, pure copper shows some desirable characteristics such as an almost perfect cube texture development, a high electrical and thermal conductivity and a diamagnetic behaviour [2, 4, 5]. Moreover, copper is not expected to poison YBCO.

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during film deposition. On the other hand, the use of a pure copper substrate for YBCO coated conductor is challenging due to the occurrence of abnormal grain growth at low temperature, the poor mechanical properties and the ease of oxidation. While the last two issues are dealt with by the cited authors, there is no investigation concerning the former, which will be addressed in the present contribution.

2. Experimental details

High purity copper bars (either electrolytic tough pitch, ETP or oxygen-free high conductivity, OFHC) were annealed for 1 h in high vacuum at 500 °C. Grain size adjustment (GSA) was performed by cold-rolling with a deformation degree above 50% and annealing in high vacuum for 10 min in the temperature range 400–500 °C. The final cold-rolling was performed using a 4-high rolling mill equipped with DLC-coated steel cylinders with a radius \( R = 24 \) mm as working rolls, reaching a deformation degree higher than 97% and a final thickness in the range 50–100 \( \mu \text{m} \). Cube texture was obtained by annealing as-rolled sample either in high vacuum or in reducing atmosphere. \( \text{La}_2\text{Zr}_2\text{O}_7 \) (LZO) film was grown on cube-textured copper substrate by metal-organic decomposition (MOD) as described by Augieri et al. [6], using a temperature plateau at 1000 °C.

Structural and morphological properties of the samples were analysed by means of X-ray diffraction and scanning electron microscopy (SEM). The X-ray \( \theta-2\theta \) and \( \omega \)-scans were performed using a Rigaku Geigerflex diffractometer working with Cu-K\( \alpha \) radiation. A LEO 1525 field emission, high-resolution SEM equipped with an Oxford INCA Crystal electron backscattering diffraction (EBSD) system was used for microstructural investigation. No tilt correction was applied. The area fraction of cube-oriented grains \( A_{\text{cub}} \) was evaluated from EBSD maps by counting the points falling within 12° from the ideal (001)[100] orientation. Cross sections were obtained by focused ion beam (FIB) technique using a FEI Helios NanoLabTM 600. A protective platinum layer (1 \( \mu \text{m} \) thick) was deposited before sample ion-milling.

![Figure 1](image1.png)

**Figure 1.** EBSD misorientation map (a) and (111) pole figure (b) of ETP Cu sample (batch B1) recrystallized for 1 h at 900 °C.

![Figure 2](image2.png)

**Figure 2.** FS-SEM image (a), EBSD misorientation map (b) and (111) pole figure (c) of OFHC Cu sample (batch A) recrystallized for 1 h at 850 °C. The lower half of the sample consists of a single, abnormal grain. In the pole figure, lower poles refer to that grain.

| Table 1. | Onset temperature of secondary recrystallization \( T_{2R} \) observed in different high-purity copper batches. |
3. Results and discussion

Cold-rolled pure copper is known to develop an almost perfect cube texture as primary recrystallization texture. In particular, it is found that a purity as low as 99.9% is good enough to obtain a sharp cube texture (Figure 1). However, abnormal grain growth caused by secondary recrystallization occurring at high temperature are often observed. The orientation of abnormal grains is in general unpredictable and they can grow as large as several mm, and even though in pure copper such grains often show an almost \{100\}<001> orientation, as shown in Figure 2, they are sometimes twinned, thus making the tape useless as oriented substrate for YBCO coated conductor. The onset temperature at which abnormal grains develop was observed is as low as 600 °C, depending on the batch, and does not seem to be correlated with the purity of raw material (Table 1). Rather, experiments indicate that the development of abnormal grains can be related to the thermomechanical process followed. In particular, it seems to depend on both the initial grain size and the thermal treatment, namely the use of a single or two-step (TSA) annealing [7]. Two different grain sizes were obtained by annealing a pre-rolled ingot for 10 min at either 400 or 500 °C (GSA). As can be seen in Table 2, the combination of low-temperature annealing of pre-rolled ingot, i.e. smaller initial grain size, and TSA with high final temperature permits to obtain fully cube textured substrates with no abnormal grain development.

On the other hand, the formation of abnormal grains seems to prevent the use of chemical solution deposition (CSD) method for buffer layer deposition on pure copper substrate, since the conversion temperature of most of the suitable buffer layer materials is typically quite high. However, the nucleation temperature of CSD oxide films is generally much lower. As an example, \( \text{La}_2\text{Zr}_2\text{O}_7 \) (LZO) deposited by MOD nucleates in the temperature range 700–750 °C [8]. As a result, LZO was successfully grown on copper substrate using batches A, B1 and B3 (Table 1, Figure 3a).

| Batch | Type   | \( T_{2R} \) (°C) |
|-------|--------|-------------------|
| A     | OFHC   | 850               |
| B1    | ETP    | > 900             |
| B2    | ETP    | 600               |
| B3    | ETP    | 850               |
| C     | OFHC   | 700               |

Table 2. Influence of the thermal treatment used in both grain size adjustment (GSA) and recrystallization two-step annealing (TSA) on the final texture of Cu OFHC (batch C) samples. \( A_{\text{cub}} \)=fraction of cube-oriented area within 12° from the ideal cube orientation; AG= occurrence of abnormal grain.
Remarkably, in several LZO/Cu samples the substrate underwent secondary recrystallization. This can be deduced by the absence of (200)Cu peak in the $\theta-2\theta$ spectrum. Nevertheless, the structural properties of LZO film are not altered by the secondary recrystallization occurred in the substrate. In fact, in the two cases (400)LZO $\omega$-scans are quite similar. Moreover, both the formation and the migration of secondary recrystallization grain boundary do not affect the LZO film, since neither cracks nor delamination could be observed (Figure 3b). This result indicates that the occurrence of abnormal grains can be neglected if the first buffer layer is deposited below the onset temperature of secondary recrystallization.

**Conclusion**

The stability of primary recrystallization in pure copper substrate was studied. It is shown that the drawbacks due to the occurrence of abnormal grains at high temperature can be avoided either by secondary recrystallization suppression by controlling the thermomechanical process, or by the use of buffer layer grown at low temperature, i.e. when secondary recrystallization will not occur. Experiments performed with MOD LZO show that grain boundary motion occurring during secondary recrystallization does not cause any delamination or crack of the buffer layer.

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