MAGNET STRUCTURE AND INTEGRATION

TASK: UT2-2005
DEVELOPMENT OF CHEMICAL DEPOSITION METHODS FOR THE FABRICATION OF YBCO HIGH TEMPERATURE SUPERCONDUCTING COATED CONDUCTORS FOR HIGH-FIELD APPLICATIONS

***Deliverable*: Processing of long length CeO_2 buffered Ni-5at.%W and Ni-5at.%W-5at.%Cr tapes for the high temperature superconducting tape fabrication**

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1. Introduction

The potential of RABiTS (Rolling Assisted Biaxially Textured Substrates) for the manufacturing of $YBa_2Cu_3O_{7-x}$ (YBCO) superconducting tapes with high transport current densities (J_c) has been demonstrated by using cube-textured Ni as a substrate. Nevertheless, pure Ni has some disadvantageous properties, which complicate the fabrication technology and, at the same time, limit the applications of the superconducting tapes. Among these, the ferromagnetism of nickel and its low tensile strength after the recrystallization are the most important ones. Therefore, lately, many efforts have been made to find the alloying elements that can suppress the ferromagnetism and enhance the strength of nickel, however preserving its cube texture. Cr and W have been chosen as alloying elements. Starting from pure Ni, different compositions in the high concentration limit of the solid solubility of these elements in nickel have been prepared. For all the three elements, i. e. vanadium, chromium and tungsten, the Curie temperature and the quality of the cube texture decrease with the increase of the alloying element concentration. It was found out that a sharp cube texture can be developed in Ni-5at%W and Ni-5at%Cr-5at%W. The deposition experiments have demonstrated that these substrates are suitable for YBCO tape fabrication. Thus, the YBCO films grown on these substrates have a critical current density of about 10^6 A/cm^2 at 77 K and zero magnetic fields.

Ceria (CeO_2) is one of the preferred buffer layers for the fabrication of coated conductors. The CeO_2 deposition process, as well as the structural and morphological properties of CeO_2 buffered Ni-W and Ni-Cr-W tapes, have been also studied. The optimization study of the deposition conditions of CeO_2 epitaxial thin films has been performed on (100) $SrTiO_3$ single crystalline substrates. CeO_2 buffered Ni-W and Ni-Cr-W tapes were used for the further deposition of the YBCO superconducting films.

2. Experimental

2.1 Alloys preparation

Ni alloys were prepared by melting the elements having a purity of about 99.95% in an argon–arc furnace with water-cooled copper hearth. The samples were melted several times in order to improve homogeneity. The as-obtained material was heat-treated in high vacuum (10^{-7} Torr) at 850°C for 12 hours. Ni-W and Ni-W-Cr bars were cold-rolled up to a thickness of about 100 μm using a conventional two-roll mill. The relative thickness reduction was between 90% and 98%. Finally, the tapes were recrystallized in vacuum (10^{-7} Torr) at 900°C.

The texture was investigated using a Seifert XRD3003 PTS diffractometer equipped with a four-circle goniometer for texture measurements. The Orientation Distribution Function (ODF) has been evaluated from the (200), (220) and (111) pole figures by means of the series expansion method.

2.2 Ceria coating solution

Several ceria coating solutions have been studied using cerium (IV) alkoxide (methoxyethoxide), acetate (III), 2,4-pentadionate (III) and basic nitrate as cerium source. 2-methoxyethanol, methanol, isopropanol were used as solvents, while glacial acetic and propionic acid, acetylacetone were used as chelating agent in the hybrid sol-gel synthesis. For the alkoxide–type precursors all the solution manipulations were carried out under argon atmosphere using standard Schlenk techniques for moisture sensitive compounds. By diluting the as purchased 18-20 % wt. cerium (IV) methoxyethoxide (Alfa Aesar) in 2-methoxyethanol, the solution was brought to a concentration of 0.2 molar. To produce the coating solution, four parts of the as-obtained solution were mixed with one part 1.0 molar H_2O in 2- methoxyethanol, resulting in a partial hydrolysis reaction.

3. Results

3.1 Deformation and recrystallization texturing of the Ni-based alloys

Every material considered in the present study exhibits a well-developed β-fiber texture, suitable for cube texturing recrystallization, which results to be stronger and sharper with an increase of the deformation degree. The Ni-W alloy has higher β-fiber ODF values as compared to both Ni-V and Ni-W-Cr. The ODF values for the three components (B, C, S) of the β-fiber have been resolved separately. The Ni-Cr and Ni-Cr-W alloys show a similar behaviour as a function of the deformation degree: the ODF values of the Brass {110}<211> (B) component of each material, relative to the total β-fiber ODF value developed on different deformations (Figure 1), increase with the increase of the deformation degree; the Copper {112}<111> (C) component shows a decrease and the S {123}<634> component remains almost constant at 35% of the β-fiber ODF value. Moreover, comparing the highest deformed samples, Ni-W still has C as the main component, while in Ni-V the B component results to be the main one for deformation degrees above about 95%. In fact, the C component

ODF values of Ni-W, relative to the β-fiber ODF value, are around 40 %. The S component of Ni-Cr shows high values up to 40%.

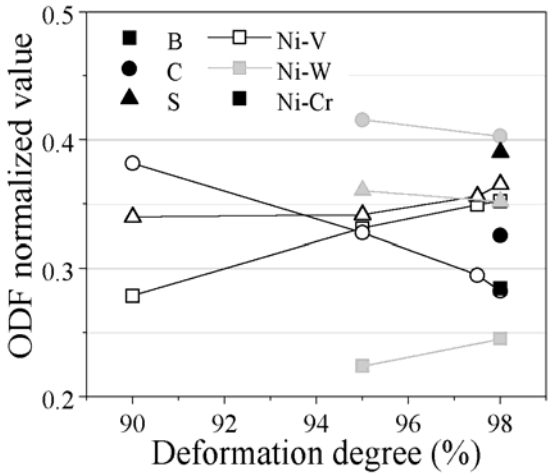


Figure 1 ODF values for B, C and S components (square, circle and triangle, respectively), relative to the total β-fibres values, vs. degree of deformation for Ni-V (open symbols), Ni-W-Cr (black) and n\i-W(gray)

During annealing, the deformation texture evolves into a cube texture. This can be seen in Figure 2, which shows the (111) pole figures for three samples annealed at (a) 600, (b) 700 and (c) 800 °C. Annealing up to 600 °C does not affect the deformation texture, since no orientation difference with respect to the as-rolled samples can be detected in the limits of the instrumental resolution. Conversely, at 700 °C a structural modification appears, with the coexistence of cube and deformation textures, since four symmetric poles at tilt angle χ=54.7° are superimposed on the preexistent texture. Finally, for temperatures higher than 800 °C the sample is cube oriented and no residual deformation texture is detectable. The only identifiable poles, other than cube, are due to {221} <122>, namely cube twins, which are intrinsically related to the recrystallization of cube grains.

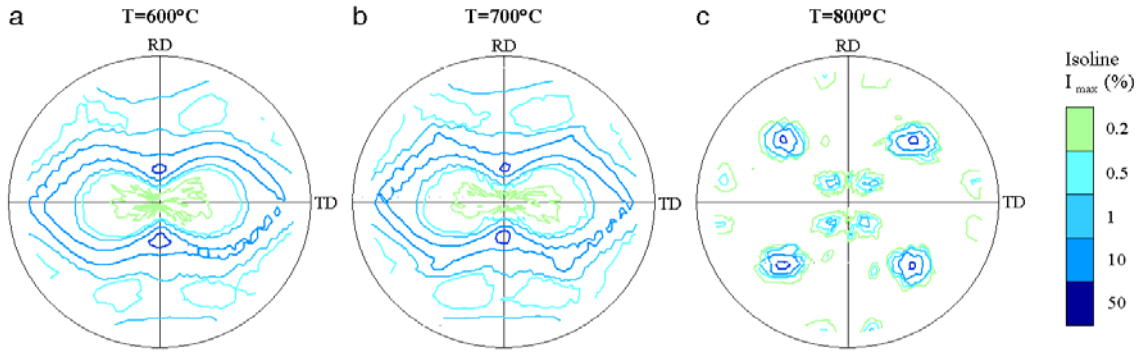


Figure 2. (111) pole figures for three Ni-W samples annealed at (a) 600, (b) 700 and (c) 800 °C and then quenched to room temperature. Non-cube reflections at 800 °C refer to {221}<122> orientations were observed.

The evolution of the recrystallization can be easily estimated with a φ-scan through the (111) pole at a tilt angle χ=54.7°, i.e. in correspondence of cube peaks positions (Figure 3). While there is a complete overlap between the distributions of the samples annealed at 600 °C and the as-rolled, the appearance of a peak at φ=45° for the sample annealed at 700 °C indicates

the beginning of recrystallization. At the same time, a consequent signal reduction for 60°<φ<90° is observable.

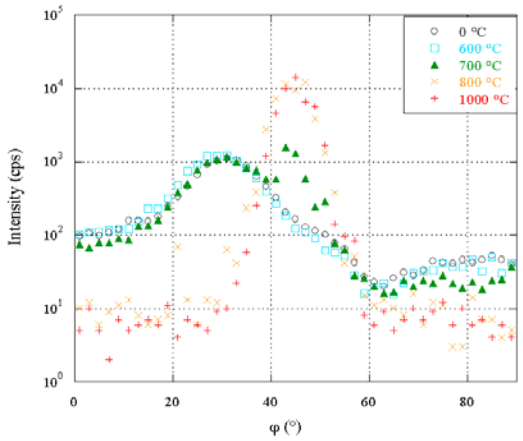


Figure 3. φ-scans at χ=54.7° for (111) pole figures of Ni-W samples annealed at different temperatures shown in figure 1. The appearance of a peak at φ=45° for the sample annealed at 700 °C indicates the beginning of recrystallization. Intensities are plotted in logarithmic scale in order to enhance low intensity reflections.

For temperatures higher than 800 °C only a peak referable to cube orientation is detectable. The full width at half maximum (FWHM) of (002)ω-scans are about 5.5° in the rolling direction and 8° in the transverse direction and (111) φ-scans of about 7°. The cube texture is found to slightly sharpen with temperature, since the FWHM of the (111) φ-scans decreases from 7.1° to 6.9° when the temperature is increased from 800 to 1000 °C. Finally, for temperatures of about 1300 °C, extensive secondary recrystallization occurs, marked by the growth of macroscopic, randomly oriented grains.

The θ-2θ measurements for samples annealed up to 600 °C reveal no changes in the peaks intensity with respect to the as-rolled and a complete recrystallization above 800 °C with the disappearance of all the peaks other than (002), while evidencing the beginning of recrystallization at 700 °C with the strong increase of the (002) peak with respect to other peaks.

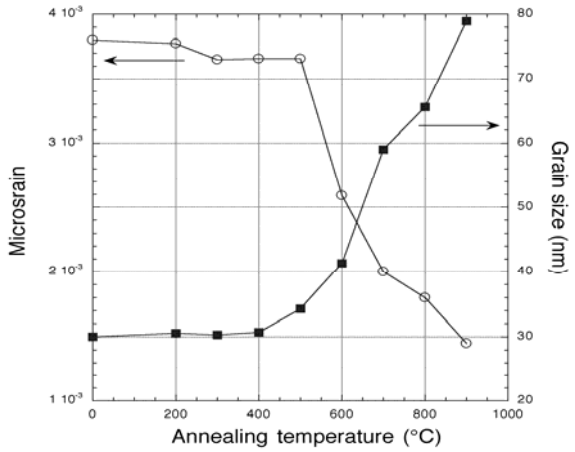


Figure 4. Evolution of microstrain (empty dots) and grain size (full squares) for Ni-W samples annealed at different temperatures and quenched to room temperature, evaluated by Monte Carlo procedure on θ-2θ diffraction peaks.

In Figure 4, the average size and microstrain of the Ni-W samples annealed at temperatures between 200 and 900 °C are shown. Up to 500 °C both microstrain and grain sizes are almost constant. Above this temperature, a decreasing of the microstrain is evident, indicating a relaxing of the defects by decreasing the dislocation density, i.e. the material begins the recovery of the lattice defects. In fact, during this stage a part of the energy stored during deformation releases through dislocations rearrangement/annihilation and subgrains formation, leading to the modification of several physical properties, such as hardness or electrical conductivity, while grains orientation remains unchanged. Further increase of the grain size above 700 °C is due to the growth of strain-free oriented grains, namely recrystallization, which is complete above 800 °C. It should be noted that the differences above 800 °C are poorly meaningful because in a fully relaxed material intrinsic peak broadening is dominant and because the algorithm could be applied on the sole (002) peak.

Signs of recovery occurrence are also visible by SEM investigations, which reveal evident microstructural modifications already at 600 °C; in fact, a fine grained structure, not detectable in the as-rolled samples, can be observed (Figure 5). Enhancing the temperature to 700 °C, a mixed deformed/recrystallized microstructure is present, with isolated cubic grains growing in the deformed matrix (figures 5a and 5b), with a density of about 170 recrystallized grains/mm^2. As can be seen in figure 5b, all the new grains are cube oriented. Moreover, the occurrence of twins is visible already in the early stage of grains formation (Figure 5b). Finally, at 800 °C the substrates are fully recrystallized and cube oriented (Figure 5c), with an average grain size of about 30 μm. The presence of grains with non-uniform size and wavy boundaries suggests that an equilibrium configuration has not been yet reached. The evolution of the recrystallization can be quantitatively appreciated through the fraction of grains falling within 15° with respect to the ideal {001}<100> orientation obtained from the EBSD measurements, which is about 3, 9, and 98% for annealing at 600, 700 and 800 °C, respectively.

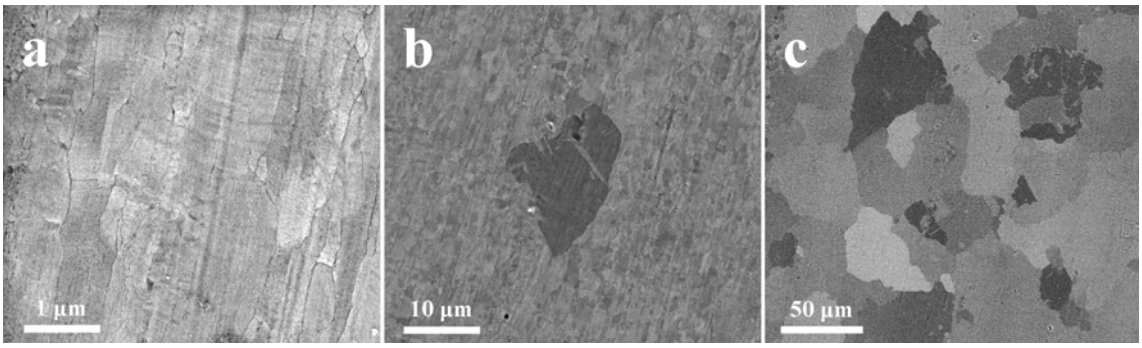


Figure 5. SE (a) and BS (b-c) SEM images of Ni-W sample annealed at (a) 600, (b) 700, and (c) 800 °C and quenched to room temperature.

From the point of view of the suitability of such substrates for coated conductors applications, microstructural stability at the typical temperatures involved in the YBCO film deposition is required. The grain growth phase through the boundary migration is much slower than the recrystallization process, since it is driven only by surface energy reduction and competition between neighboring grains and is promoted as temperature and time increase. In order to study the grain growth evolution with time, different samples have been annealed at 900 °C for a time ranging from 0 to 4 h. This annealing temperature has been chosen since it is slightly higher than YBCO deposition temperature, namely 850 °C, while promoting

a complete substrate recrystallization. EBSD and SEM analyses were performed in the same region before and after a thermal treatment at 850 °C for 30 minutes (the same as that used at the deposition of YBCO film) in order to observe grain boundary migration and its possible correlation with grains orientation.

Recrystallization with no temperature plateau leads to noticeably shallow grain boundaries, though rather unstable; in fact, several grain boundaries migrate due to the subsequent simulation treatment. A low-angle (i.e. smaller than 15°) grain boundary migration occurring among three neighboring cube-oriented grains can be seen in Figure 6.

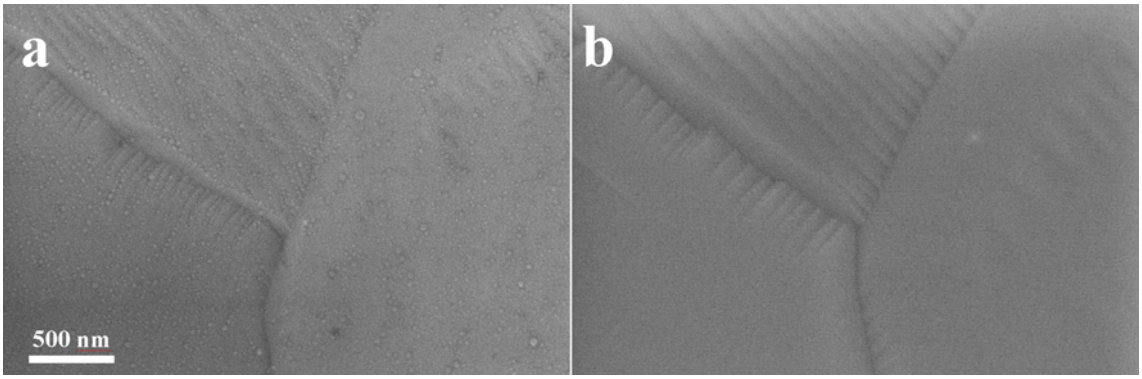


Figure 6. SE-SEM images at the same magnification of a Ni-W sample recrystallized at 900 °C with no plateau, before (a) and after (b) simulation treatment at 850 °C for 30 minutes. Low-angle grain boundary migration can be estimated.

Interestingly, the effect of additional annealing leads to more pronounced facets present on the surface of the upper grain as well as at the boundaries. This feature is found to appear commonly, though not systematically, on cube textured substrates and seems to be particularly enhanced by high temperature.

Another microstructural modification occurred is visible in figure 7, since the small grain *D* shrank due to the growth of *A* and *B* grains.

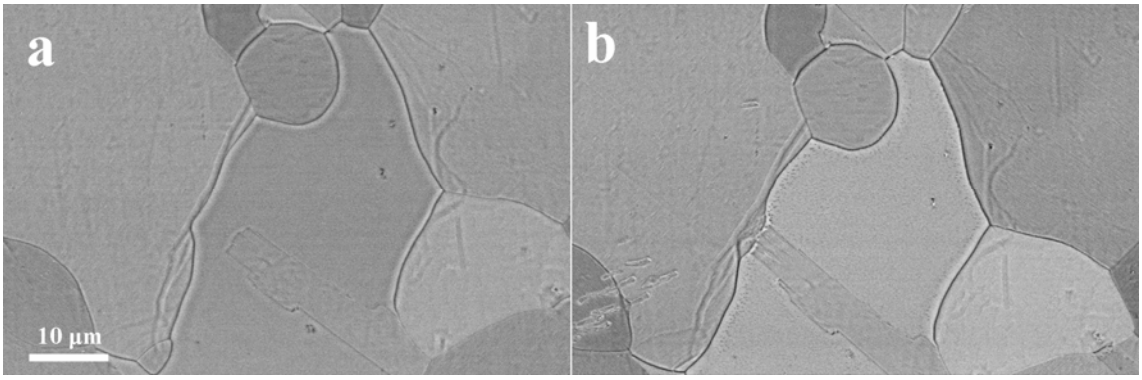


Figure 7. BS-SEM images at the same magnification of a Ni-W sample recrystallized at 900 °C for 5 minutes, before (a) and after (b) simulation treatment at 850 °C for 30 minutes.

In samples recrystallized at 900 °C for 20 minutes the grain boundary migrations occur only in correspondence of high-angle boundaries and for distances below 0.5 µm. Finally,

the samples subjected to longer annealing, namely 900 °C for 1 and 4 hours develop a fully stable microstructure after the simulation treatment.

As can be seen from figure 8, Ni-V, Ni-Cr-W and Ni-W heat treated at 900 °C for 4 hours present a sharp cube texture with the ϕ-scan FWHM of the (111) poles of 9°, 8° and 6°, respectively, weakly dependent on deformation degree above 95%. The twinned cube texture ODF values are qualitatively in agreement with the twinned cube grain fraction obtained from the optical microscope analysis.

Figure 9 presents the SEM micrographs of the studied Ni-based substrates. The surfaces of all the analyzed substrates are quite smooth. As can be observed, the Ni-V and Ni-Cr substrates have a greater concentration of twinned cube textured and misoriented grains respect to the Ni-W ones. The twins have a quasi-rectangular shape and are perpendicular to each other, corresponding to the (111) and $(1\bar{1}1)$ twinning planes. The rough aspect of the surface is caused by the grooves developed at the grain boundaries. As observed by optical microscopy, the grooves are related to the boundaries of twinned cube textured and misoriented grains. A direct correlation between the number of twinned cube textured and misoriented grains has been observed, suggesting the same origin of the controlling factors. The mean grain size of the Ni-V and Ni-W-Cr recrystallized analyzed alloys is of about 23 μm, while for Ni-W is of about 29 μm.

From the optical microscope analysis, the fraction of the twinned cube textured grains for Ni-V, Ni-W-Cr and Ni-W was estimated to be of about 0.17, 0.15 and 0.05, respectively. Nevertheless, the ratio of the area representing cube-oriented grains to the substrate area is 0.96, 0.97 and 0.99, with accuracy within 2%.

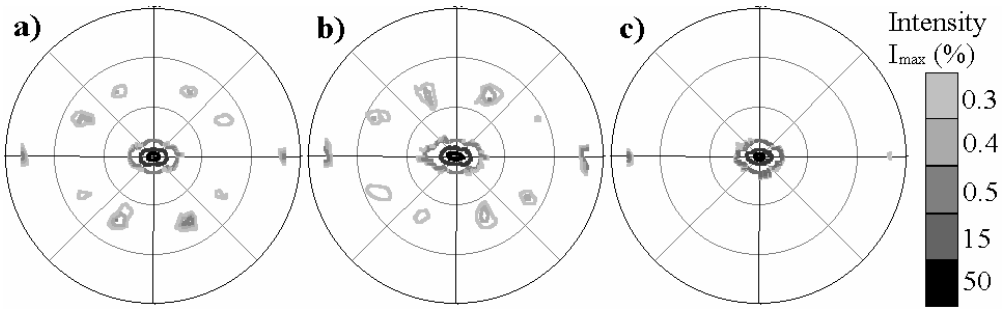


Figure 8. (002) polar figures of $Ni_{89}V_{11}$ (a), Ni-5at%W-5at%Cr (b) and $Ni_{95}W_5$ (c) tapes recrystallized at 900°C for 4 hours in vacuum (10^{-7} Torr); isolines are set in order to underline the presence of twins.

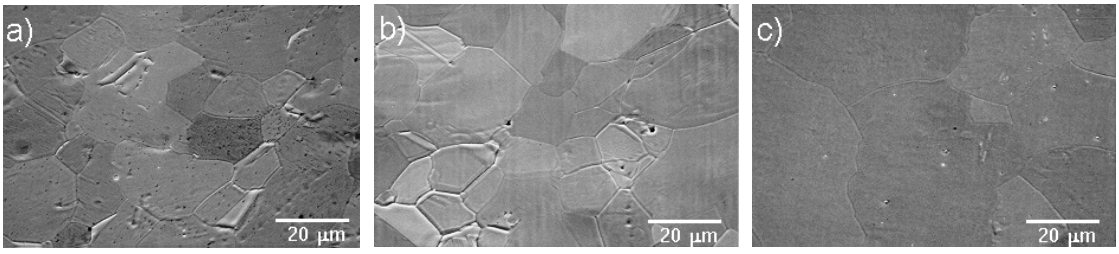


Figure 9. SEM micrographs of Ni-V (a), Ni-W-Cr (b) and Ni-W (c) tape surfaces

4. Deposition of CeO2 films on Ni-W substrate by chemical method

The optimization study has revealed that the best results were obtained using the coating solution obtained from cerium (IV) methoxyethoxide in 2-methoxyethanol 0.2 molar. The optimum treatment treatment temperature is 1000 ^{0}C under flowing Ar-4%H_2 mixture.

The θ-2θ scans for the CeO_2 films grown at 900°C and at 1000°C for 1h in 4%H_2/96%Ar atmosphere show only (200) and (400) CeO_2 peaks, no other CeO_2 reflections are detected. This demonstrates that the CeO_2 films are epitaxially grown with an $[h00]//[h00]$ epitaxial relationship between the substrate and the film. The ω-scan of (200) CeO_2 peak has a Full-Width-Half-Maximum (FWHM) of 0.5° and 0.3° for the sample thermally treated at 900°C and 1000°C, respectively (Figure 10).

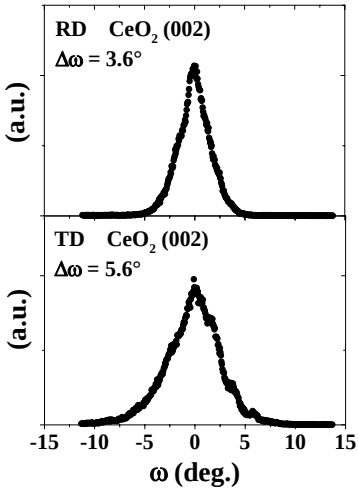


Figure 10. Rocking curves for the (200) peak of CeO_2 on Ni-W substrate

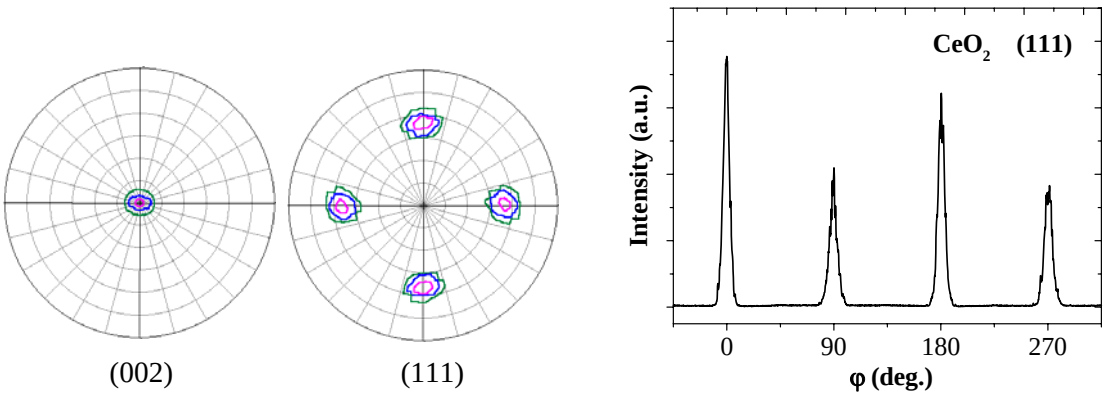
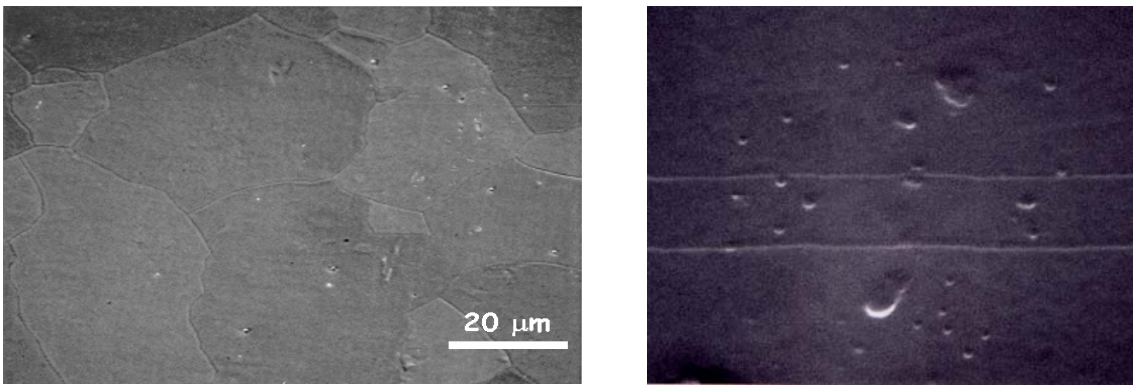


Figure 11. (002) and (111) pole figure of 500 nm CeO_2 film on $Ni_{95}W_5$ substrate and φ-scan (111); in pole figures equilines are in logarithmic scale.

The in-plane orientation was analyzed by pole figures and ϕ scans. Figure 11 presents the (200) and (111) CeO_2 pole figures. The presence of a well developed single component cube texture is evident. The in-plane crystallographic relationship between the substrate and the CeO_2 film is [111]Ni-W ||[100]CeO_2.

The SEM studies of the CeO_2 film have revealed a uniform, smooth and crack-free CeO_2 surface as it can be observed from Figures 12a and b. The film exhibits a smooth and crack-free surface (Figure 12b). The cross-section SEM studies have shown that the films have dense microstructures, without cracks or porosity. Moreover, the as deposited films exhibit a uniform microstructure over the substrate grain boundary, indicating a good coalescence of the CeO_2 film grown on the Ni-W substrates. This has a positive influence on the transport properties of the subsequently deposited YBCO film. The CeO_2-Ni-W interface is smooth and is a replica of the substrate morphology. Taking into account these observations and the structural analyses, one can conclude that the oxidation resistance of the Ni-W substrate is high enough to permit a good epitaxial deposition of CeO_2 .



(a) (b)

Figure 12. SEM micrograph of the CeO_2 film on the Ni-W substrate. Low magnification (a) and high magnification (b), respectively.

4. Conclusions

Finally, we can conclude the following:

The cube texture development of cold rolled Ni 5 at% W alloy and its stability at the typical temperatures of YBCO film deposition by PLD have been investigated. The X-rays analyses for a series of samples annealed at different temperatures reveal that the cube texture is promoted at 700 °C and at 800 °C is fully recrystallized. X-ray, EBSD and SEM analyses confirm this behavior and evidence that at 600 °C recovery occurred. Microstructure stability has been evaluated through a series of recrystallized samples held at 900 °C for variable time. The microstructure is found to be unstable when annealing without a temperature plateau, with both low- and high-angle grain boundaries migration. In samples annealed from 5 to 20 minutes only high-angle grain boundaries migration is observed, while low-angle grain boundaries remain pinned. Finally, the microstructure is found to be stable within 1 hour annealing. The preliminary results on YBCO deposition, both by chemical and physical methods on Ni-based substrates, have demonstrated that these substrates are adequate for coated conductors manufacturing. The as deposited YBCO film exhibits a high critical current density of about 1 MA/cm^2 at 77 K and self magnetic field.

The structural and morphological properties of CeO_2 on Ni and Ni-W biaxially textured metallic substrates have demonstrated that the chemical deposition method is appropriate

for the epitaxial deposition of CeO_2 on Ni based alloys. Moreover, the properties of the CeO_2 films are adequate for further deposition of YBCO superconducting films.

5. Foreseen activities and results for 2006

The activities for 2006 will be mainly focused on chemical methods for YBCO deposition on metallic substrates for the development of coated conductors fabrication technology. The fulfil this, the following objectives have been established:

- The preparation of an adequate coating solution with long shelf life for the high quality epitaxial deposition of YBCO films
- The optimization of the thermal treatment for the deposition of high critical current density YBCO films on CeO_2/YSZ/CeO_2 buffered Ni-W biaxially textured substrates

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