Cube textured CeO$_2$, BaZrO$_3$ and LaAlO$_3$ buffer layers on Ni based Substrates

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Abstract. CeO$_2$, BaZrO$_3$ as well as LaAlO$_3$ buffer layers were deposited on \{100\}<001> Ni + 5 weight-% W substrates by a wet chemical technique. The solutions were prepared by dissolving the metal nitrates or acetates and zirconiumacetylacetonate, respectively, in mixtures of acetic acid, methanol and water. The solutions were applied by dip- or spin-coating, dried at 135 °C and annealed at temperatures between 900 and 1 400 °C depending on the buffer layer for 15 min. under Ar-5% H$_2$ gas flow. Pole-figure measurements proved the exact texture of each buffer layer. Electron microscopy showed dense and smooth buffer layers.

1. Introduction

Research on superconductors for the transport of electric energy is currently focusing on "coated conductors". These coated conductors are (textured) metallic tapes, frequently first coated with buffer layers and then with superconducting layers. The buffer layer should protect the substrate against oxidation during the sintering process of the superconducting layer and should reduce the lattice mismatch between the substrate and the superconductor. The technological challenge for the production of long-length coated conductors is to find a low-cost, easily scaleable process for the fabrication of high quality substrates and buffer layers. The RABiTS (Rolling Assisted Biaxially Textured Substrate) technique is one approach to solve these problems [1, 2]. A sharp cube texture can be produced by rolling and by re-crystallization of a Ni tape. Biaxially textured buffer layers are then commonly deposited onto the nickel substrate by high vacuum techniques. Current research focuses on the application of buffer layers from solution to avoid costly vacuum based processes.

In this paper we report on the preparation of CeO$_2$, BaZrO$_3$ and LaAlO$_3$ buffer layers onto \{100\}<001> Ni + 5 weight-% W substrates from different solutions via spin- and dip-coating followed by suitable heat-treatment [3, 4].

2. Experimental

The \{100\}<001> textured nickel (Ni + 5 weight-% W) substrates were supplied by Plansee (Austria). The substrates were cut into pieces of 10 mm x 5 mm. The substrates were first cleaned in an ultrasonic bath with a mixture of chloroform, acetone and methanol, then etched in a boiling mixture of aqueous 30 % H$_2$O$_2$ and formic acid (1 + 1 by volume) to improve the wetting of the substrate surface with the different precursor solutions. A cleaning step in methanol completed the substrate pre treatment [5].
Solutions for the preparation of CeO$_2$ were prepared by mixing a 4 M aqueous Ce(NO$_3$)$_3$ solution with methanol (1 + 1). Solutions for the formation of BaZrO$_3$ were prepared by dissolving zirconium acetylacetonate and barium acetate in a glacial acetic acid - methanol mixture (1 + 1). The concentration of the BaZrO$_3$ precursor solution was about 1 M. Solutions for LaAlO$_3$ layers were prepared by dissolving La(NO$_3$)$_3$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O in water. The volume of the solution was then adjusted with methanol. The concentration of the solution was about 1 M. Small amounts of triethanolamine were added to all solutions in order to improve the adhesion of the precursor solutions to the substrate.

The different precursor solutions were applied to the pre-treated cube textured nickel substrates either by spin- or by dip-coating. A speed of 5 000 rpm and a holding time of 20 seconds were used in the spin coating process. The coated samples were then dried at 135 °C for 10 minutes. Annealing was carried out at 1 160 °C for CeO$_2$, at 900 °C for BaZrO$_3$ and at 1 400 °C for LaAlO$_3$ in a tube furnace for 15 min in flowing Ar-5% H$_2$.

X-ray diffraction (XRD) studies with Ni-filtered Cu-K$_\alpha$ including pole-figure measurements were carried on an XPert instrument (Panalytical). The surface roughnesses of the substrates were analyzed by atomic force microscopy (Digital Instruments, Dimension 3100). The microstructure and the thickness of the films were investigated by scanning electron microscopy (SEM) on a Röntec instrument (Röntec, Germany).

3. Results and discussion

Pole-figures and the ODF analyses confirmed the very sharp cube texture of the Ni + 5 weight-% W tapes. The pretreated substrate surface had a surface roughness of about 29 nm.

3.1. CeO$_2$ buffer layers

The phase formation and the texture formation on the substrates were investigated as a function of the temperature in an Ar-5% H$_2$ atmosphere for duration of 15 min.

![Figure 1: Left: X-ray patterns of CeO$_2$ on {100}<001> textured Ni + 5 weight-% W, sintered at different sintering temperatures for 15 minutes. Right: pole figure of CeO$_2$ on {100}<001> textured Ni + 5 weight-% W sintered at 1 160 °C for 15 minutes.](image)

Sintering temperatures below 1 160 °C did not result in textured CeO$_2$ layers. At 1 160 °C a very sharp biaxial texture is formed. Heat treatment above 1 160 °C reduced the texturing of the CeO$_2$ buffer layer. No impurity phases were observed in the X-ray patterns (Figure 1). Pole figure analysis showed a biaxial texture of the CeO$_2$-crystallites on the {100}<001> textured nickel. The ODF analysis (Figure 2) confirmed that the (h00) planes of the CeO$_2$ layers were parallel to the substrate surface and that the CeO$_2$ crystallites are rotated by 45° to the rolling direction of the substrate. Rotating of the CeO$_2$ crystallites by 45° decreases the misfit between the Ni substrate and the buffer.
The ODF analysis also proved that the deviation of the orientation depends on the sintering temperature. For a temperature of 1 160 °C the deviation is around ± 4° (FWHM 4°) and for 1 200 °C the deviation is around ± 7° (FWHM 7°).

**Figure 2**: ODF-analyses of CeO$_2$ on {100}<001> Ni + 5 weight-% W (left: sintered at 1 160 °C, right: sintered at 1 200 °C). The ODF’s was calculated from the (111) und (200) pole-figures.

Scanning electron microscopy revealed the continuous, dense, smooth and crack-free microstructure of the buffer layers obtained from spin-coating of the precursor. Spin coated layers were generally slightly better than dip coated layers.

### 3.2. BaZrO$_3$ layers

Heat-treatment below 900 °C did not result in textured BaZrO$_3$ layers. At 900 °C the X-ray diffraction indicates a high degree of a texture. Higher temperature did not improve the quality of the BaZrO$_3$ layers. No impurity phases were observed in the XRD spectrum (Figure 3). The ODF-analysis showed the biaxial texture of the BaZrO$_3$-crystallites. The (h00) planes of the BaZrO$_3$ buffer layer were parallel to the substrate surface. One part of the crystallites grew along the axes of the substrate and the other part of the crystallites grew with 45° twisted around the c-axes onto the cube textured substrate. Thus in-plane texturing consisted of two crystallite orientations.

**Figure 3.** Left: BaZrO$_3$ on {100}<001> Ni + 5 weight-% W. (A: sinter temperature 800 °C and B: sinter temperature 900 °C). Right: ODF-analyses of BaZrO$_3$ on {100}<001> Ni + 5 weight-% W. The ODF was calculated from the (110) und (200) pole-figures.
3.3. LaAlO₃ layers
The texture analysis showed that a biaxially textured LaAlO₃ layer was formed on {100}<001> textured nickel. The ODF-analysis and the pole-figure proved that the (h00) planes of LaAlO₃ buffer were parallel to the substrate surface and that the crystallites grew along the a-b axes of the substrate. A small amount of the crystallites is twisted by 45° (Figure 4).

![Figure 4](image.png)

**Figure 4.** ODF-analyses of LaAlO₃ on {100}<001> Ni + 5 weight-% W. The ODF was calculated from the (010) und (110) pole-figures.

![Figure 5](image.png)

**Figure 5.** Scanning electron micrograph of a cross section of a spin-coated CeO₂ layer on Ni. The concentration of the precursor solution was 2 M.

3.4. Film thickness of the buffer layers
To determine the film thickness of the different buffer layers, cross sections was prepared. For 2M CeO₂ precursor solutions, the film thickness was about 200 nm (Figure 5). For 1 M BaZrO₃ and LaAlO₃ precursor solutions, the film thickness was about 100 nm. Generally a linear dependence of the film thickness on the solution concentration was observed.

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