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The effect of substrate surface nature on texture formation in nickel oxide

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X-ray diffraction was used to study the influence of surface finishing on polycrystalline nickel and its modification with ultra-fine dispersions of CeO_2 on crystallographic texture development in NiO scales, grown at 1073 K in 760 torr oxygen for time periods up to 75 h. Ni substrate characterized by $\{1\,0\,0\}\langle 0\,2\,3\rangle$ texture and surface with an atomic structure revealed by chemical polishing led to the formation of NiO with $\{1\,0\,0\}\langle 0\,1\,3\rangle$ texture, indicating an epitaxial growth. After applying CeO_2 on the Ni surface prior to the oxidation, no essential changes in NiO texture were detected. When the Ni surface was deformed by mechanical polishing, NiO exhibited a fibre texture with a major component of $\langle 1\,1\,0\rangle$ oriented along the growth direction. The presence of CeO_2 on this substrate changed the dominant fibre axis to $\langle 1\,0\,0\rangle$. The texture data are discussed in terms of the oxide microstructures and their growth kinetics. In particular, for CeO_2-modified NiO scales with complex depth structure, the possible contribution of individual sublayers to the overall measured texture is estimated. © *1998 Kluwer Academic Publishers*

1. Introduction

The importance of cold work and surface finishing in oxidation of polycrystalline nickel was well documented in earlier studies by Graham *et al.* [1, 2]. Since the higher growth rate of NiO on cold-worked Ni compared to annealed Ni, observed especially at temperatures between 773 and 1073 K, was accompanied by finer oxide microstructure, the authors concluded that grain boundaries in NiO acted as "short circuit" paths for the diffusion of ionic species. Our recent experiments revealed that substrate surface finishing also exerted a crucial influence on the oxidation behavior of Ni, when superficially modified with reactive elements or their oxides. Although the presence of 14 nm CeO_2 derived from sol–gel markedly reduced the oxidation rate of mechanically polished Ni, the oxide still grew faster than that found for uncoated Ni with a substrate finished by chemical polishing [3]. Moreover, the effectiveness of a reactive element as a function of exposure time, evaluated from a change in the instantaneous rate constants, was decreasing with time for the mechanically polished substrate [4].

In order to estimate the contribution of grain boundary diffusion to oxide growth, in addition to grain boundary density, their structure should be taken into account. For oxidation of pure Ni, the importance of grain boundary characteristics is clearly seen from the experiments on single crystal faces [5]. The crystallographic structure of grain boundaries seems to be even more important for NiO modified with a reactive element. Here, the grain boundaries may not only act as easy diffusion paths for metal and oxygen ions, but also as paths for ions of the reactive element. In this way, they affect the stability of reactive element concentration inside NiO as well as its effectiveness [6]. It is obvious that a crystallographic texture is a basic indicator of grain boundary character in polycrystalline material [7]. Therefore, the objective of this study is to assess the role of surface finishing of polycrystalline nickel substrate and its modification with ultra-fine dispersions of CeO_2 in texture development in NiO layers.

2. Experimental

The material used for oxidation was 0.8 mm thick nickel foil of 99.5% purity, supplied by Johnson Matthey (Ward Hill, MA). Cold-rolled coupons with a size of 15×25 mm were at first annealed in flowing argon atmosphere at 1173 K for 1 h. Two techniques of surface finishing were then employed: (i) mechanical polishing with 1 μm diamond paste and (ii) chemical polishing at room temperature in a solution consisting of 65 ml acetic acid, 35 ml nitric acid, and 0.5 ml hydrochloric acid. Coatings were deposited by dipping the cold substrate in high purity sol containing 5 g dm^{-3} of CeO_2 [3]. After deposition, the coatings were dried at room temperature for about 20 h and converted to nanocrystalline ceramics by calcination at 573 K for 1 h. The oxidation was performed in a quartz tube furnace at 1073 K in pure oxygen at 760 torr pressure.

The oxide phase composition was examined using an X-ray Rigaku diffractometer with rotating anode

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and CuK$_\alpha$ radiation. Textures of Ni substrate and oxides were measured using a D-500 Siemens X-ray goniometer. Pole figures were obtained using the reflection technique up to a maximum tilt of 80 deg in 5 deg polar and radial intervals. The results were corrected for absorption and defocussing using a standard random specimens prepared from Ni or NiO powder. For morphological observation of oxide growth surfaces, a scanning electron microscopy (SEM) was used.

3. Results

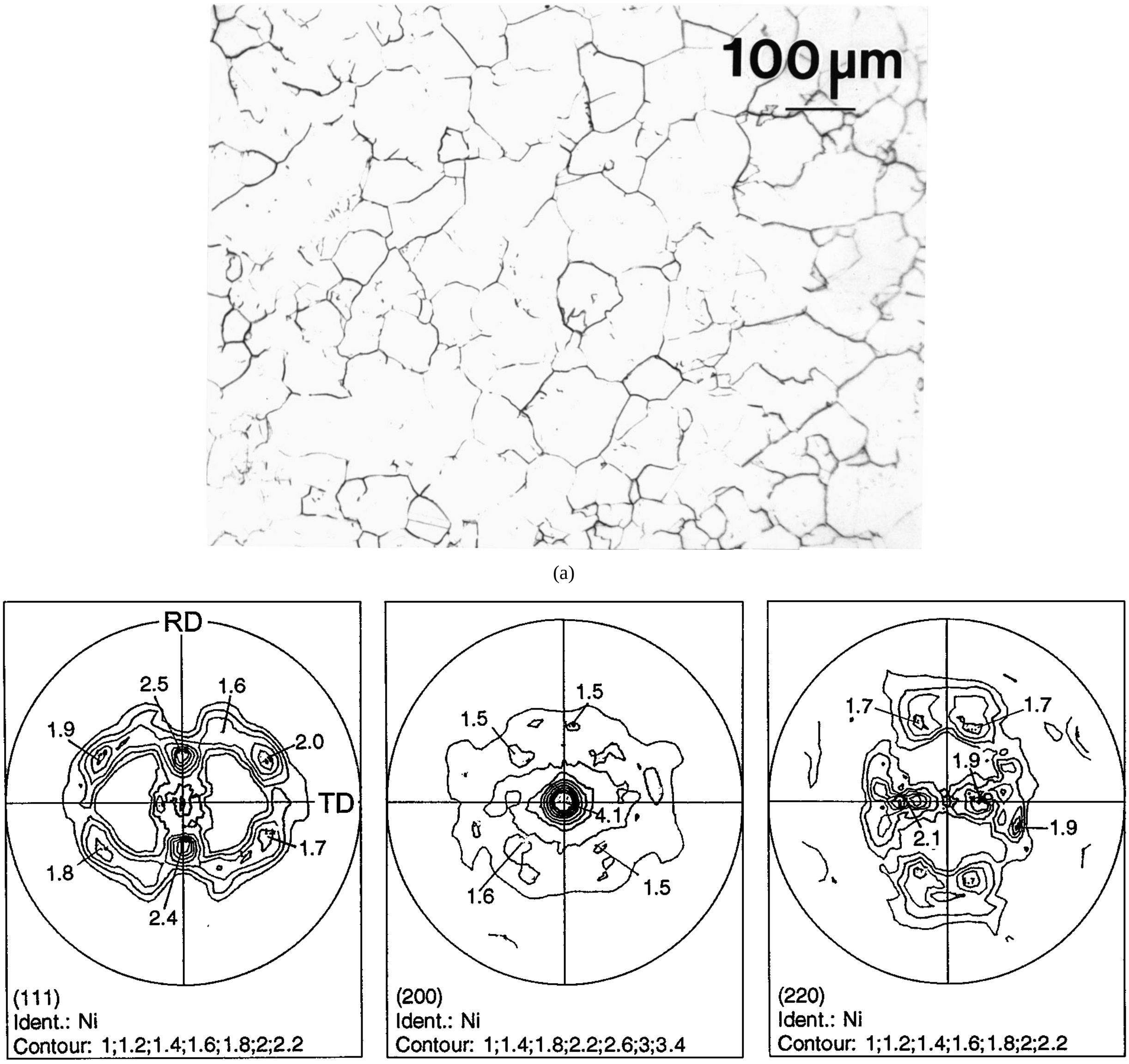
3.1. Characterization of polycrystalline Ni substrate

The polycrystalline cold-rolled nickel after annealing at 1173 K for 1 h exhibited the microstructure shown in Fig. 1a with an average grain size of 100 μm. According to X-ray measurements, the orientation of nickel grains was characterized by $\{1\,0\,0\}\langle 0\,2\,3\rangle$ texture with a maximum intensity of 4.1 times random (Fig. 1b). The surface of such Ni specimens was modified before oxidation. The purpose of chemical polishing was to remove the thin film of oxide formed during argon-annealing and to reveal an atomically clean surface with the arrangement of atoms, specific for the crystallographic orientation of each grain. Conversely, to suppress the influence of crystallographic orientation of the individual Ni grains, the surface of Ni was mechanically polished lightly using a 1 μm diamond paste. This treatment produced on the substrate surface an uniformly deformed metallic film.

3.2. Phase analysis of the oxides

No influence of the substrate surface finishing was detected on the phase composition of the oxides grown during subsequent exposure to oxygen. In general, a single NiO phase was grown on pure Ni (Fig. 2a). On CeO_2-coated substrate, in addition to NiO phase, some traces of CeO_2 were found (Fig. 2b). No mixed compounds, however, between Ni, O and Ce were formed.

It should be noted that all the oxides were totally penetrated by X-rays, which is evident from the presence



(a)

(b)

Figure 1 Optical micrograph showing grain size (a), and pole figures characterizing texture (b) of polycrystalline Ni substrates after argon-annealing at 1173 K for 1 h.

of the substrate peaks on the diffraction scans. The transmission of whole thickness by X-rays is important to texture measurements of CeO_2-modified oxides, where some complex depth-structures are expected. Thus, for those structures, all the individual sublayers contributed to the pole figures measured. Moreover, the X-ray diffraction patterns show that all the major peaks of NiO i.e., (1 1 1), (2 0 0), and (2 2 0) are clearly separated from the other peaks for Ni or CeO_2. As a result, no interference is expected during texture measurement when using an X-ray texture goniometer.

3.3. Texture and morphology of NiO grown on chemically polished substrates

As previously described [1–4], the oxide growth on chemically polished Ni was highly anisotropic. It is obvious that NiO morphology and thickness depend on the Ni grain orientation and on the type of Ni grain boundary (Fig. 3a). Application of 14 nm thick CeO_2 coating did not essentially affect the NiO growth anisotropy. This means that the Ni face orientation and type of Ni

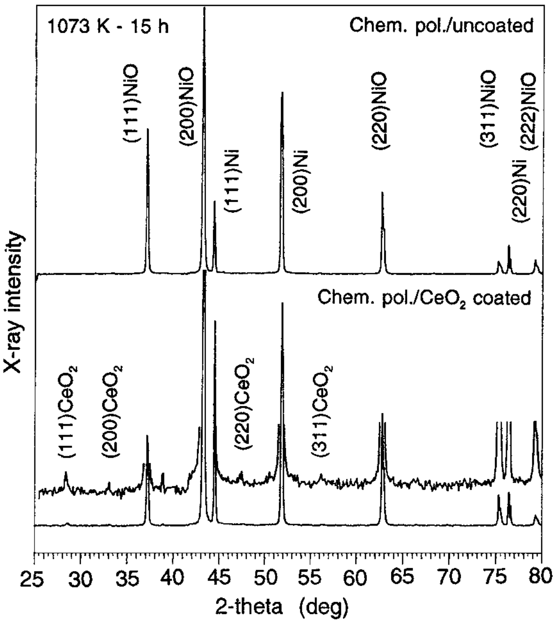
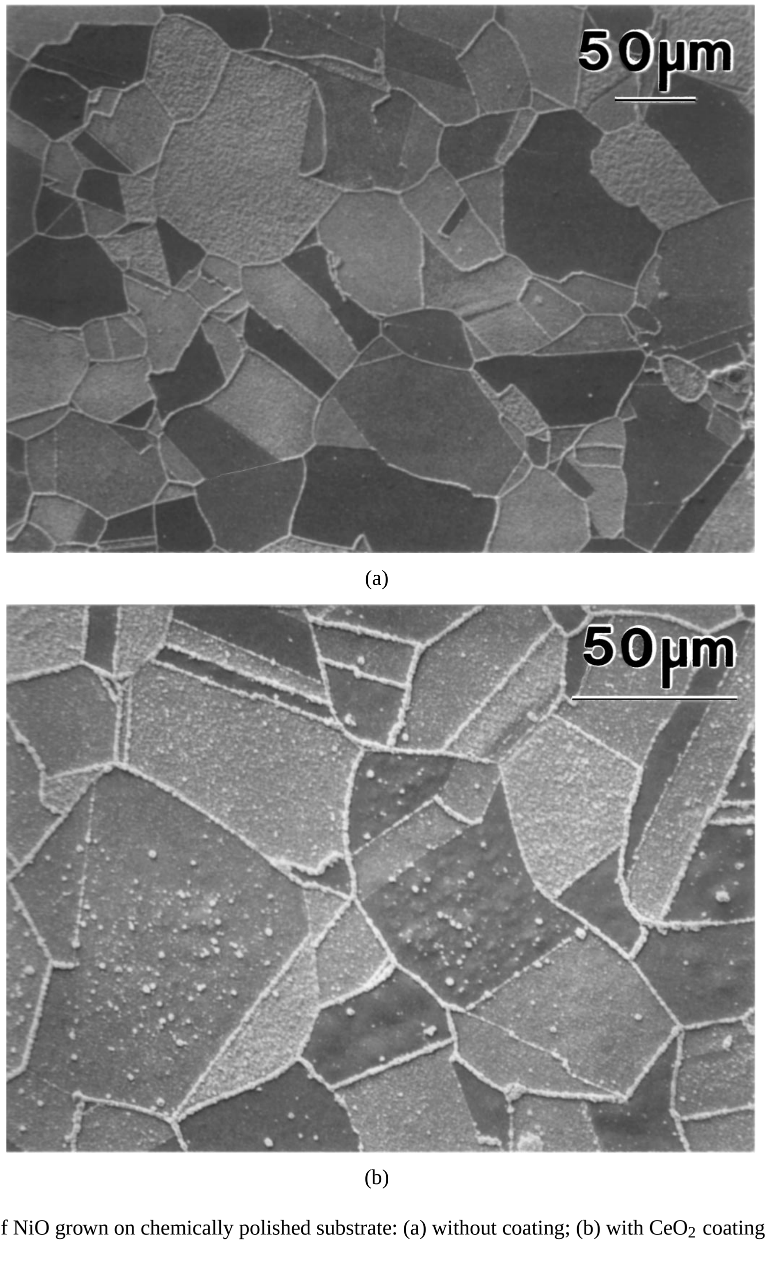


Figure 2 X-ray diffraction patterns, characteristic for NiO grown on pure and CeO_2-coated Ni (CuK_α radiation).



(a)

(b)

Figure 3 SEM morphology of NiO grown on chemically polished substrate: (a) without coating; (b) with CeO_2 coating (1073 K, 5 h).

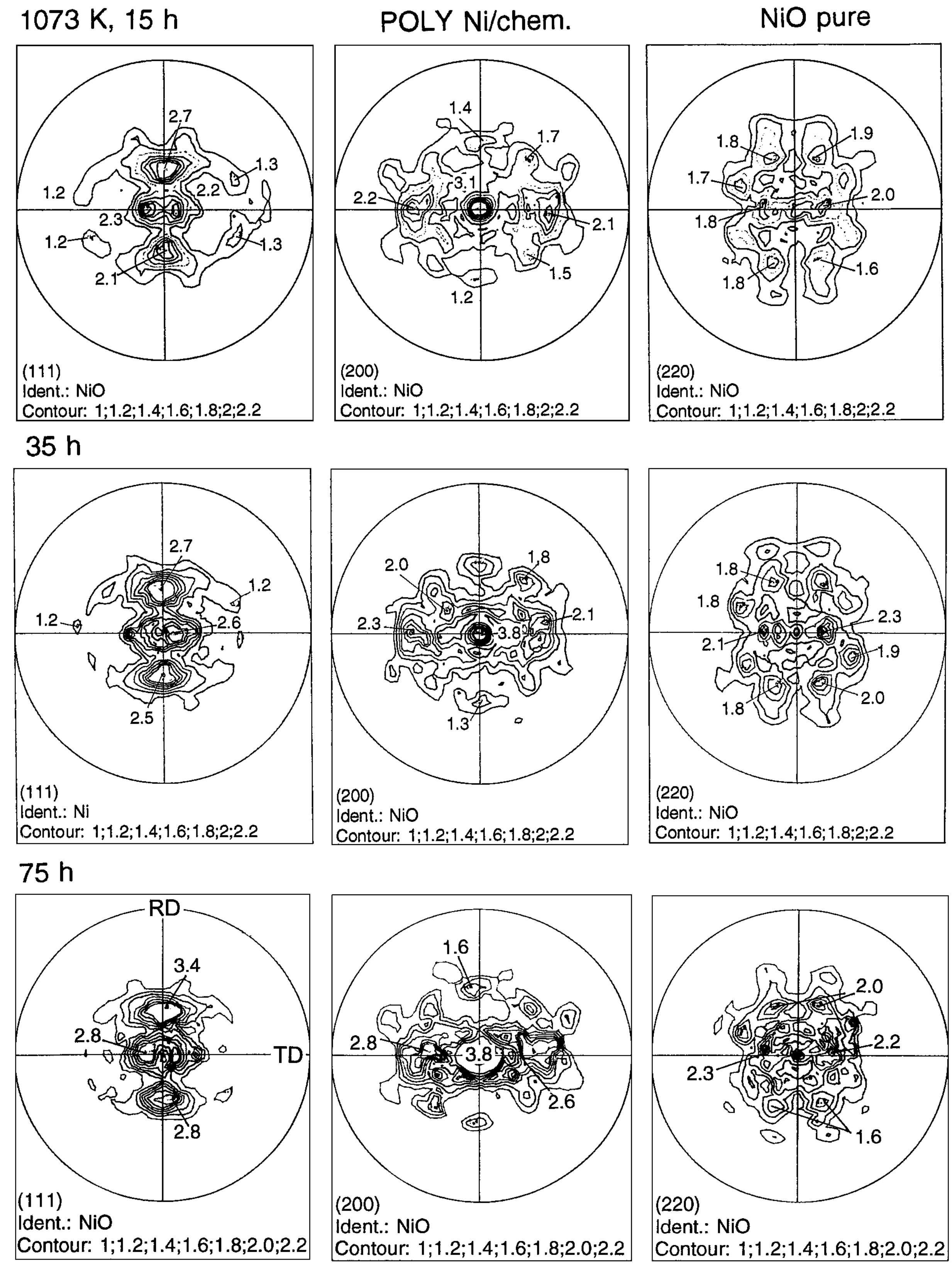


Figure 4 Pole figures of NiO grown at 1073 K for 15, 35 and 75 h on pure Ni finished by chemical polishing.

grain boundaries still exerted the crucial effect on the oxidation process (Fig. 3b).

The texture of NiO formed on chemically polished Ni is represented by three basic pole figures in Fig. 4. In order to compare the substrate and oxide textures, the sample was oriented in the same way as during measurements of Ni texture (Fig. 1b). The corresponding rolling and transverse directions of Ni are indicated. Analysis of the pole figures shows that NiO exhibits a $\{1\,0\,0\}\langle 0\,1\,3\rangle$ texture, very similar to that present in the Ni substrate. Thus, the comparison of pole location on pole figures of Ni and NiO and the crystallographic relationships between Ni and NiO lattice, observed previously for single crystalline Ni substrates [8, 9], suggest

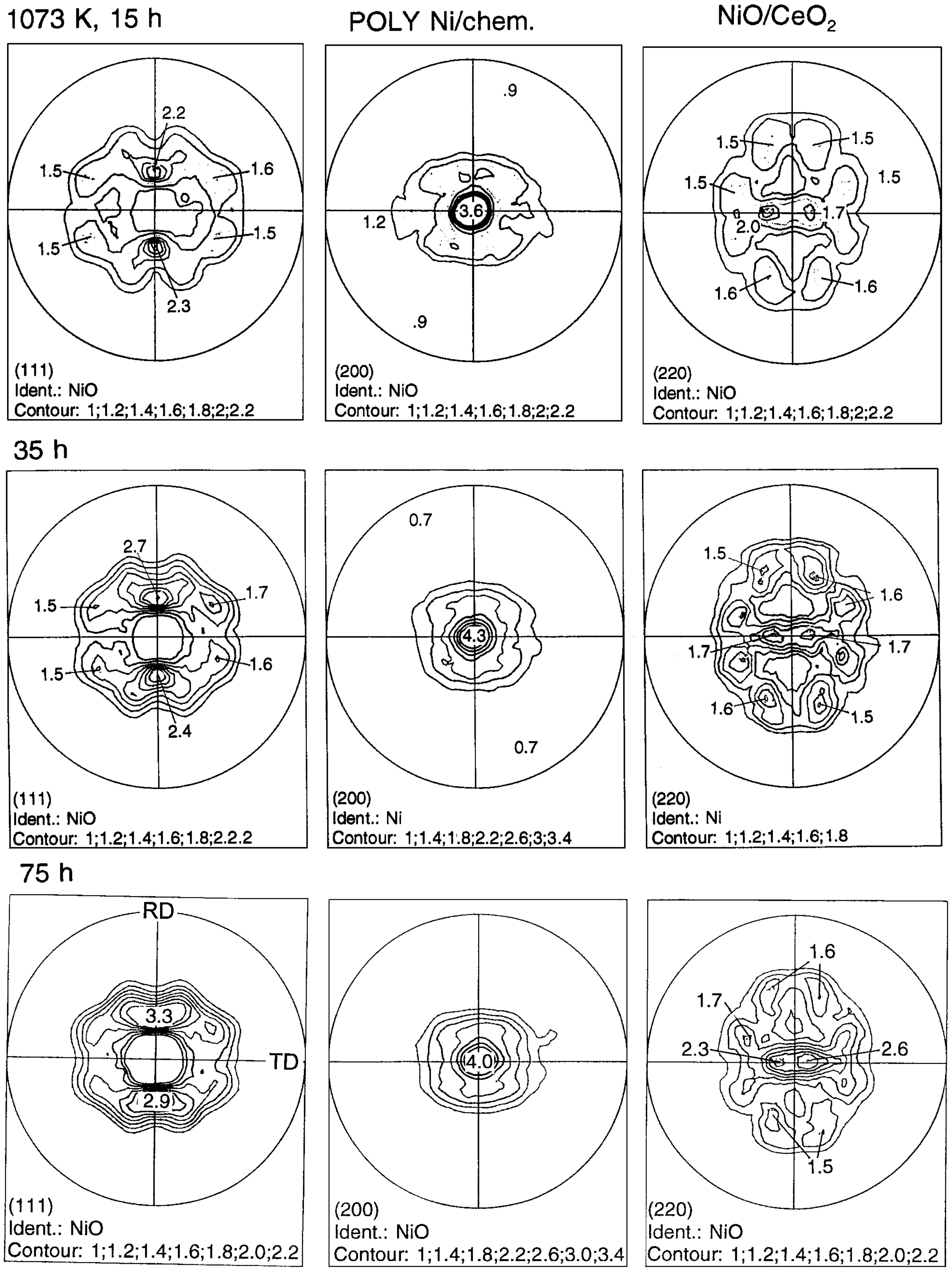
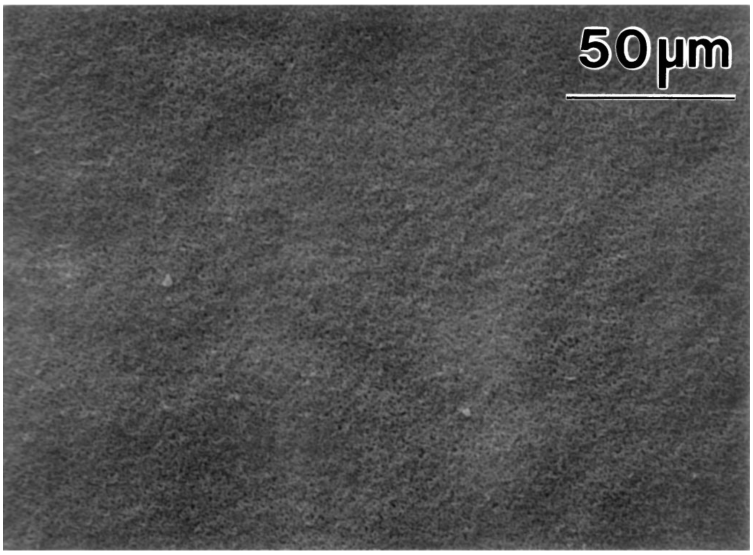


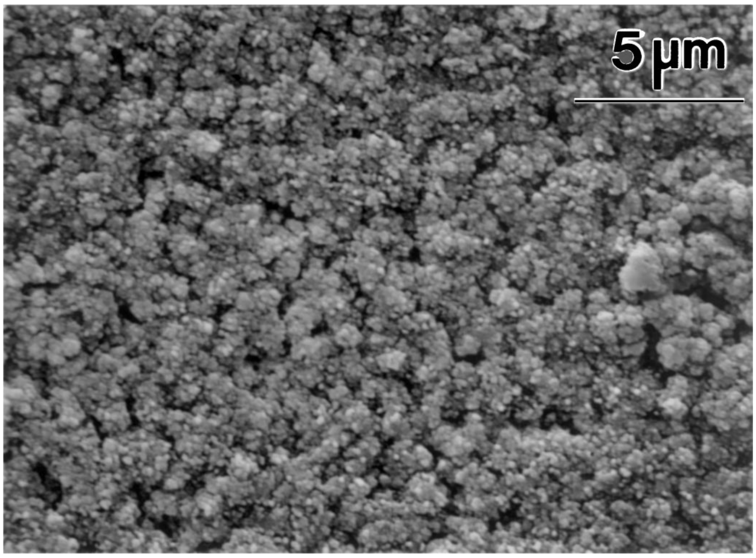
Figure 5 Pole figures of NiO grown at 1073 K for 15, 35 and 75 h on CeO_2-coated Ni finished by chemical polishing.

the epitaxial character of the oxide grown after 15 h exposure. A further oxidation of up to 35 h did not change the NiO texture. The shape of contour lines on pole figures, however, seems to suggest the diminishing contribution of the epitaxy during oxide thickening. In addition, the maximum intensity on (2 0 0) pole figures increased from 3.1 to 3.8 times random and remained at that level up to a period of 75 h of oxidation.

It is surprising that the application of CeO_2 coating did not essentially change the NiO texture. As seen in



(a)



(b)

Figure 6 SEM morphology of oxide grown on mechanically polished substrate: (a) without coating; (b) with CeO_2 coating (1073 K, 5 h).

Fig. 5, the clear contour lines on pole figures suggest an even stronger influence of the substrate than that observed in the absence of coating. In addition, the maximum intensities of 3.6–4.3 are higher than previous ones and practically meet those measured for Ni.

3.4. Texture and morphology of NiO grown on mechanically polished substrates

In contrast to NiO grown on chemically polished Ni, after mechanical polishing, the NiO was uniform in thickness and in morphology over the entire surface (Fig. 6a). No influence of substrate grain orientation or the type of substrate grain boundary on oxide growth was observed. The same was essentially true for CeO_2-coated Ni (Fig. 6b). Thus, the major influence of the reactive element was the refinement of NiO grains, which exhibited a "cauliflower like" morphology [3].

The different morphology of the oxide was accompanied by a different texture (Fig. 7). In general, no similarity with the substrate texture, indicating an epitaxy, was found. The NiO grown on pure Ni showed a fibre texture with the major component of $\langle 1\,1\,0\rangle$ oriented along the growth direction, and had an intensity of 3.5 times random. This intensity decreased to 2.6, and further to 2.5, after 35 and 75 h exposure, respectively. The changes on (1 1 1) and (2 0 0) pole figures with oxidation time show the growing importance of $\langle 1\,0\,0\rangle$ fibre component for thicker scales. At this point however, it is difficult to explain the deviation of $\langle 1\,0\,0\rangle$ poles from the pole figure centre (growth surface normal).

The presence of the reactive element coating changed the NiO texture. As seen in Fig. 8, after 15 h of growth, the pole figures exhibit a $\langle 1\,0\,0\rangle$ rough fibre. The shape of contour lines, suggesting some influence of the substrate, should probably be attributed to the changes of Ni-substrate surface during deposition of CeO_2 coating. One suspects that the plastically deformed surface layer, obtained as a result of mechanical polishing, was affected by acidic nature of CeO_2 sol and the subsequent thermal treatment at 573 K for 1 h. A further exposure produced a clear $\langle 1\,0\,0\rangle$ fibre, and the maximum intensity of (1 0 0) poles increased continuously up to 3.7 times random after 75 h oxidation.

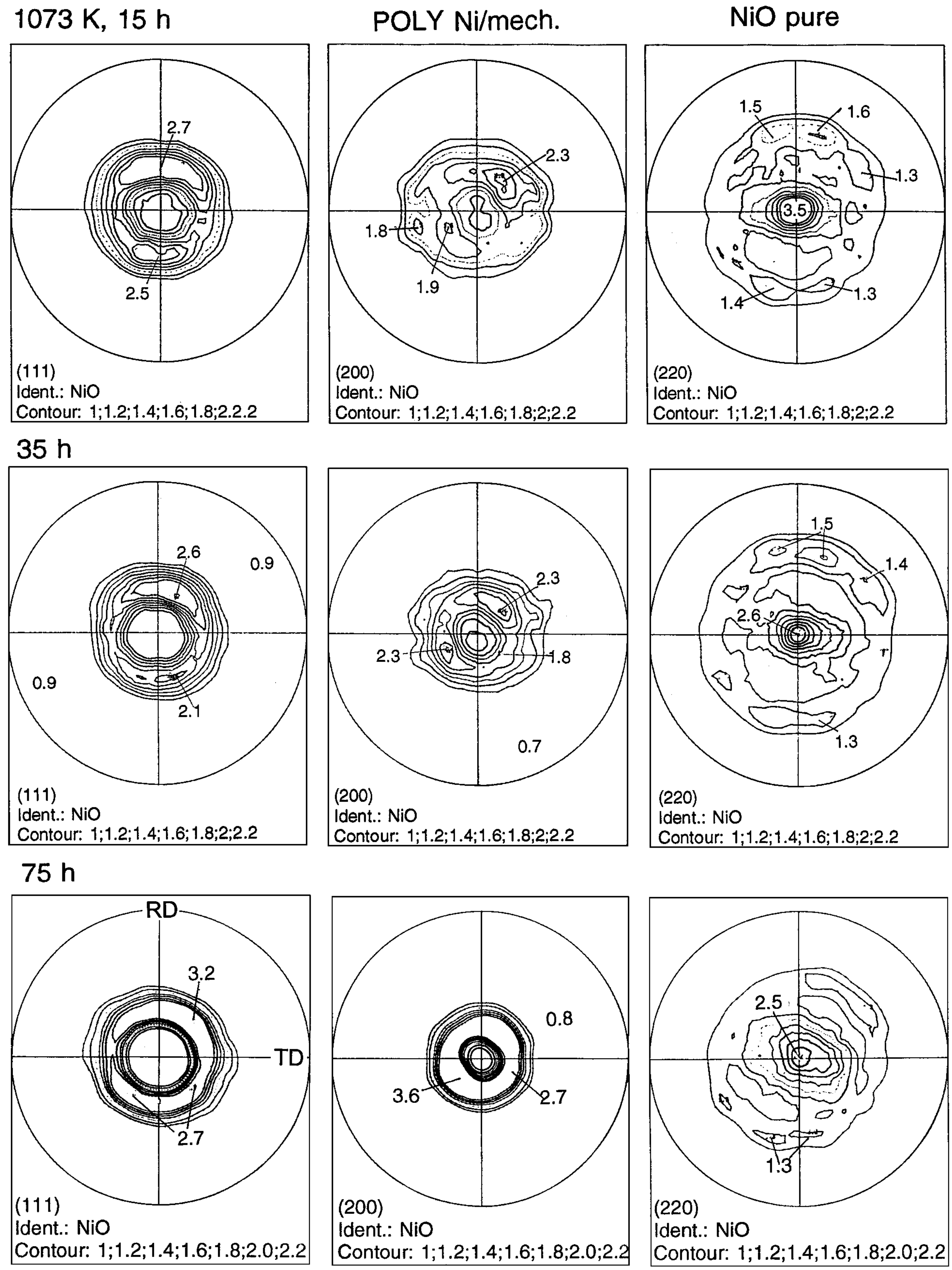


Figure 7 Pole figures of NiO grown at 1073 K for 15, 35 and 75 h on pure Ni finished by mechanical polishing.

4. Discussion

The measurements performed in this study reveal the essential differences in textures of oxides grown on individual Ni substrates. These differences are accompanied by changes in oxidation kinetics, depth location of the reactive element, and evolution of surface topography, as reported in details previously [3, 4, 10]. In order to correctly interpret the texture data, they should be compared with the corresponding depth microstructures of the oxides.

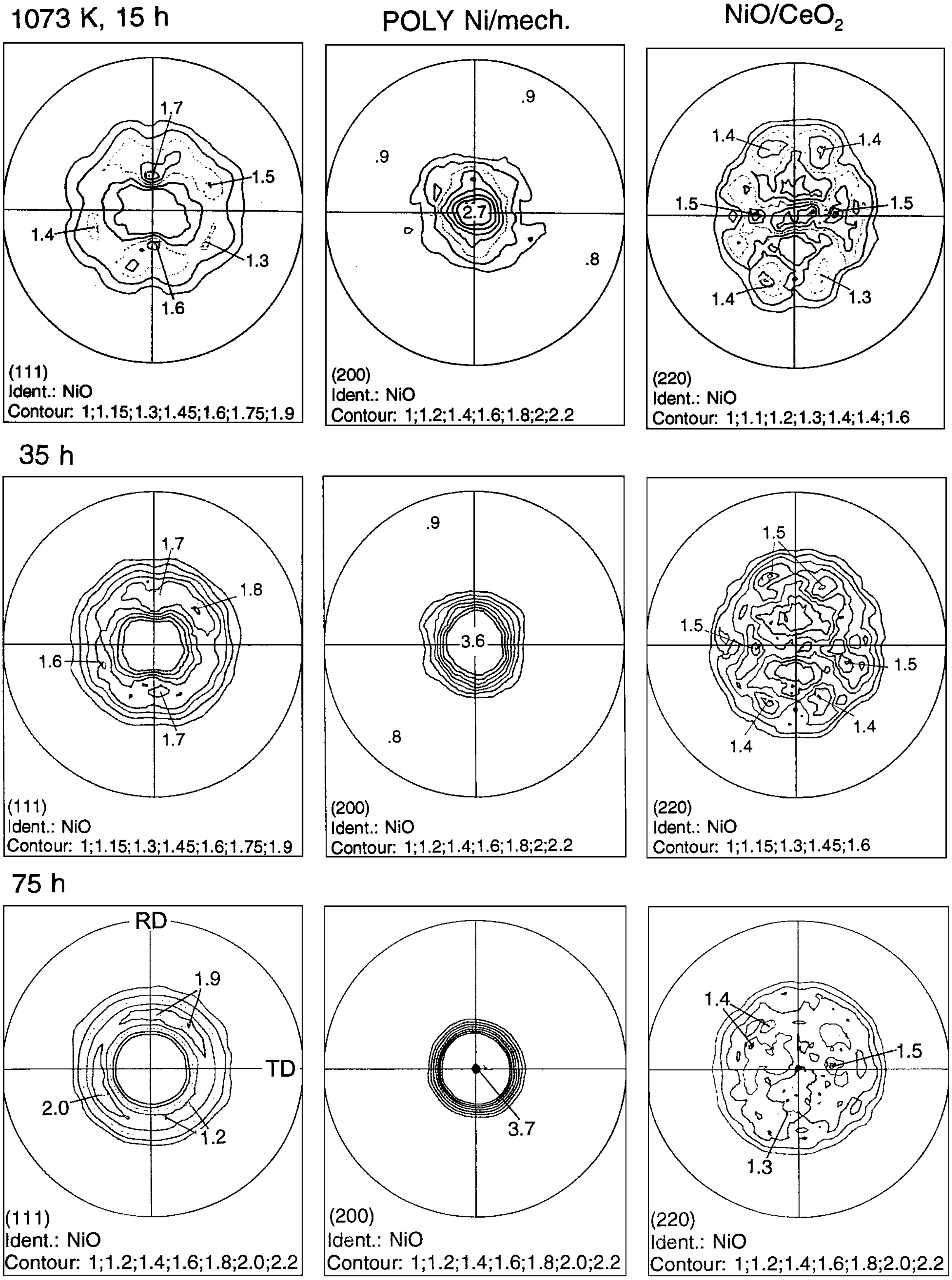
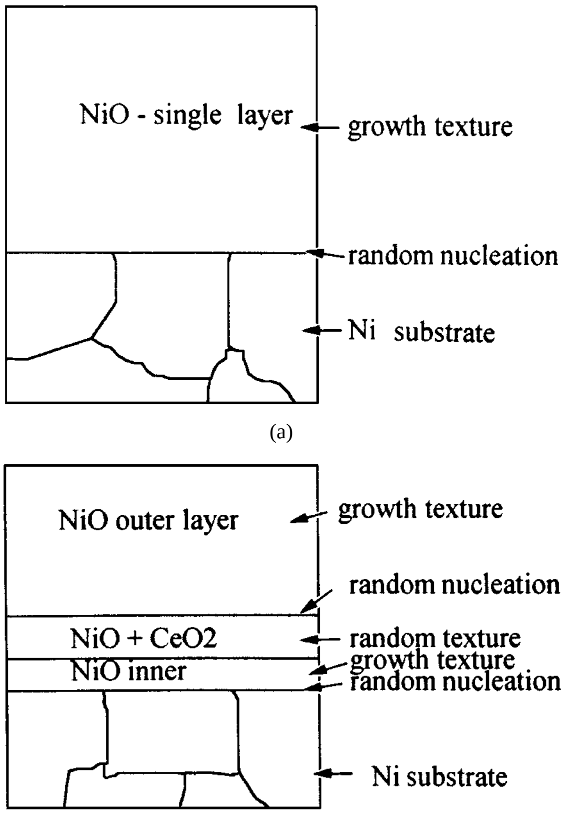


Figure 8 Pole figures of NiO grown at 1073 K for 15, 35 and 75 h on CeO_2-coated Ni finished by mechanical polishing.

Of all the substrates studied, the simplest oxide microstructure was developed on mechanically polished Ni (Fig. 9a). When CeO_2 is absent, at the beginning, the fine and randomly oriented oxide grains nucleate on the deformed surface of Ni. After a few minutes' exposure, however, there are signs of formation of the preferred orientation, as shown elsewhere by TEM electron diffraction [4]. The pole figures of oxides formed during longer exposures exhibit evident growth texture (Fig. 7), apparently unrelated to the substrate texture



(a)

(b)

Figure 9 Schematic representation of the cross sectional microstructures of NiO formed on Ni mechanically polished: (a) without coating; (b) after coating with CeO_2.

(Fig. 1). The major texture component observed here, a ⟨1 1 0⟩ fibre, was also detected by other authors [11] in thick NiO scales formed at 1373 K. Although some possibilities to develop the duplex structures exist for thick NiO scales and are believed to be caused by the inward transport of molecular oxygen [12], according to SEM imaging of fracture cross-section, for temperature and time range of this study, the single NiO layer existed and contributed to the X-ray diffraction signal.

The presence of CeO_2 coatings on mechanically polished Ni leads to the more complex depth structure of the oxide (Fig. 9b). After oxidation, CeO_2 is present in a well-defined two-phase layer composed of NiO and CeO_2 [3]. Thus, the X-ray signal was diffracted from all three sublayers. While the texture of the middle layer is apparently random [3], both the inner and outer layers are characterized by specific preferred orientations. After the oxidation of mechanically polished and coated Ni, the CeO_2-containing part is located deep inside the oxide [13, 14]. In such a structure, the outer layer, being thicker, has a higher contribution to X-ray signal diffracted. It can be concluded therefore that the outer layer is characterized by a ⟨1 0 0⟩ fibre texture with strength increasing with oxidation time (Fig. 8).

In order to follow the formation of the three-layer structure of oxide shown in Fig. 9b, one should remember that the CeO_2 particles in the coating are randomly oriented, as is the first layer of NiO nucleated on top of the coating [15]. At a steady stage of oxidation, two growth fronts are active: at the oxide–gas interface and beneath the CeO_2 rich part. According to the oxygen isotope experiment [14], however, the predominant reaction front is at the oxide–gas interface, with the growth dominated by outward diffusion of Ni cations (Fig. 9b). The oxide texture measured on this substrate was therefore developed during growth from a randomly nucleated NiO film on CeO_2 coating.

The literature suggests that during outward growth, the oxide grains do not change their orientation and that the texture must result rather from the growth selection. According to Khoi *et al.* [16], the preferential absorption of oxygen at the oxide surface could be a decisive factor in that mechanism. An alternative hypothesis, suggested by Chadwick and Taylor [11], is based on the lower surface energy of (1 0 0) planes, as NiO has a preferred cubic habit. The results of this study show that CeO_2 affected the development of NiO-growth texture on mechanically polished Ni (Figs 7 and 8). Since no CeO_2 particles are present inside the outer layer, one may suspect that Ce ions diffusing along NiO grain boundaries could contribute to the changes observed. In fact, the presence of some ion segregants in outer layer of NiO formed on mechanically polished Ni was detected by some authors [11, 13].

The texture of pure NiO grown on chemically polished Ni should be considered a sum of textures developed on individual Ni grains. In general, oxide texture depends on Ni substrate orientation, and a number of specific epitaxial relationships is given in the literature [16]. According to our X-ray measurements, oxidation of (1 1 1)Ni face leads to the growth of NiO characterized by a single component (1 1 1) texture. In NiO grown on (1 0 0)Ni, there is present a ⟨1 1 1⟩ fibre in addition to (1 0 0) epitaxial component [5, 9]. The comparison of pole figures of Ni substrate and NiO layers (Figs 1 and 4) shows that oriented nucleation and epitaxial growth dominate the oxide texture development on chemically polished Ni. The same conclusion could be drawn from the oxidation of chemically polished Ni substrate with another texture characteristic for extruded rod [17].

The development of NiO texture on chemically polished Ni starts in the same way as for mechanically polished Ni. Namely, the presence of CeO_2 leads to random nucleation of NiO on top of the coating at the beginning of oxidation, as was shown by TEM electron diffraction [18]. As soon as the CeO_2-modified NiO layer is formed, the growth mechanism of oxide changes from outward Ni to inward oxygen ion diffusion [14]. As a result, the dominant reaction front moves underneath the CeO_2-containing layer, and Ni orientation again plays an important role in NiO growth, the same when CeO_2 coating was absent. In this process, the inner NiO layer increases predominantly its thickness [4, 10] and finally contributes to the textures measured. This explains, why the textures of the NiO layers grown on chemically polished Ni, both pure and CeO_2 coated, do not exhibit substantial differences.

5. Conclusions

1. Surface finishing of polycrystalline nickel exerted a critical effect on texture of both pure and CeO_2-modified NiO grown at 1073 K in 760 torr O_2.

2. Oxidation of uncoated, Ni with a {1 0 0}⟨0 2 3⟩ texture and an atomic structure of the surface revealed by chemical polishing, led to oriented nucleation and the epitaxial growth of NiO with a final {1 0 0}⟨0 1 3⟩ texture. The presence of CeO_2 coatings on this substrate caused a random nucleation of NiO during the initial stages of growth, though it did not substantially change the texture of thick NiO layers formed at a steady stage of reaction.

3. Plastic deformation of Ni surface by mechanical polishing, in the absence of CeO_2, resulted in random nucleation of NiO and development of ⟨1 1 0⟩ fibre growth texture. Deposition of CeO_2 coatings on plastically deformed Ni surface also led to the nucleation of randomly oriented NiO at the beginning of oxidation. The CeO_2 coating did, however, change the growth texture of thicker NiO scales on this substrate to a ⟨1 0 0⟩ fibre.

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