Structure and Oxidation Behavior of Nickel Nanoparticles Supported by YSZ(111)

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ABSTRACT: Nickel nanoparticles supported by the yttria-stabilized zirconia (111) surface show several preferential epitaxial relationships, as revealed by in situ X-ray diffraction. The two main nanoparticle orientations are found to have their [111] direction parallel to the substrate surface normal and ~41.3 degrees tilted from this direction. The former orientation is described by a cube-on-cube stacking at the oxide–metal interface and the latter by a so-called coherent tilt strain-relieving mechanism, which is hitherto unreported for nanoparticles in literature. A modified Wulff construction used for the 111-oriented particles results in a value of the adhesion energy ranging from 1.4 to 2.2 J m⁻², whereby the lower end corresponds to more rounded particles and the upper to relatively flat geometries. Upon oxidation at 10⁻³ Pa of molecular oxygen and 673 K, a NiO shell forms epitaxially on the [111]-oriented particles. Only a monolayer of metallic nickel of the top (111) facets oxidizes, whereas the side facets seem to react more severely. An apparent size increase of the remaining metallic Ni core is discussed in relation to a size-dependent oxidation mechanism, whereby smaller nanoparticles react at a faster rate. We argue that such a preferential oxidation mechanism, which inactivates the smallest and most reactive metal nanoparticles, might play a role for the long-term degradation of solid oxide fuel cells.

INTRODUCTION

Supported nanoparticles are used on a tremendously large scale for catalytic reactions. Due to the inherent inhomogeneity of these, often industrial, materials, the basic understanding of their exact atomic structure and relation to their functionality can become very complex. One route to overcome this problem is by design of so-called bottom-up experiments in which well-defined nanoparticles are subjected to controlled environments. Such studies can be performed by depositing nanoparticles in ultrahigh vacuum on perfect single crystal substrates, after which their structure is characterized under different thermodynamic conditions and gas environments. In this way, for example, oxidation–reduction-induced reversible shape changes in nanoparticles have been discovered. Solid oxide fuel cells (SOFCs) are devices used for energy conversion and are considered as an important future green technology. Their function is largely dependent on catalytic processes taking place at their interfaces. Two important chemical reactions between the surrounding gas atmosphere and the solid play a decisive role. At the cathode, oxygen is dissociated, and the ions enter the electrolyte. Fuel is being oxidized at the anode side, for which the required oxygen reaches the interface through the solid electrolyte. Both the cathode and the anode consist of complex materials having a large surface area, such as polycrystalline oxides (cathode) or nickel nanoparticles (anode). Usually, Ni is grown on the electrolyte by wet-chemical methods.

Here we investigate Ni nanoparticles (NPs) deposited on a polished yttria-stabilized zirconia (YSZ) substrate as SOFC model anode by surface sensitive X-ray diffraction methods. YSZ with 9.5 mol % Y₂O₃ content is a widely used SOFC electrolyte material because of its high oxygen ion conductivity. Nickel films grown on MgO(100) have been found to show several preferential orientations, forming a complex epitaxial system and of which the core is stable toward high temperature oxidation. This raises the question how smaller particles in the size regime from 3–10 nm, as typically encountered on the anodes of SOFCs behave when in contact with a solid electrolyte. Their sintering behavior in different atmospheres is particularly important for catalytic activity and long-term stability. Here we show the results of such a study, whereby the Ni NPs are first annealed and finally oxidized. We find that Ni nanoparticles grow with two very distinct orientations on YSZ(111), in contrast to MgO(100). The NiO formed during oxidation grows epitaxially with respect to the Ni nanoparticles. From the measured particle heights and widths, the energy of adhesion, which is an important quantity with respect to the nanoparticles’ sintering stability, is determined.

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structures. The Ni NPs were grown with a substrate which was found to result in smooth and well-defined surface structures. The Ni NPs were grown with a substrate temperature of 623 K at a growth rate of 0.2 nm/min resulting in a nominal 3 nm of deposited material. Here, we present results from two such growth runs with different samples, named sample I and sample II hereafter. For sample I, only the as-prepared NPs were structurally characterized, and after the in situ synchrotron experiment, the sample was investigated by atomic force microscopy (AFM) in air. In a second experiment on sample II, the Ni NPs were further treated, and extensive X-ray characterization was carried out. The as-prepared Ni NPs were first annealed at 973 K for 75 min, then exposed to $10^{-3}$ Pa of O$_2$ for 120 min, a procedure which was found to result in smooth and well-defined surface structures. The Ni NPs were grown with a substrate temperature of 623 K at a growth rate of 0.2 nm/min resulting in a nominal 3 nm of deposited material. Here, we present results from two such growth runs with different samples, named sample I and sample II hereafter. For sample I, only the as-prepared NPs were structurally characterized, and after the in situ synchrotron experiment, the sample was investigated by atomic force microscopy (AFM) in air. In a second experiment on sample II, the Ni NPs were further treated, and extensive X-ray characterization was carried out. The as-prepared Ni NPs were first annealed at 973 K for 75 min, then exposed to $10^{-3}$ Pa of methane at 573 K for 30 min and finally oxidized at $10^{-3}$ Pa of O$_2$ at 573 K for 35 min. After each of these steps, extensive X-ray data were taken, which allow us to determine changes in the orientation, size, and composition of the NPs. Because the methane exposure did not result in any notable structural changes, these data are not included in the present report. In addition, at each of the sample preparation steps, the YSZ surface structure was investigated by measuring several CTRs with a nonzero in-plane momentum transfer. These data do not indicate any considerable changes after Ni evaporation and after the oxygen treatment. Because these CTRs probe the 3D atomic structure of the YSZ(111) surface, which is partly covered by the NPs, we conclude that each of these processing steps does not result in any significant atomic relaxations of the substrate.

## RESULTS

**Surface Morphology, Coverage, and Nanoparticle Height.** AFM images were taken ex situ after the first growth run of nickel nanoparticles on YSZ(111) without further treatments (sample I). The resulting image is shown in Figure 1. Particles are clearly observed, and typical heights of 3 nm can be derived. Just after growth, with the sample still in the UHV chamber, X-ray reflectivity (XRR) measurements were taken (see Figure 2 together with the XRR curves from sample II described more extensively in this paper). The curves of the as-prepared states in both experiments are very similar. Analysis of the XRR data is performed by fitting the electron density profile along the surface normal $Q_{\theta} = 4\pi \sin(\theta) / \lambda$, with $\theta$ half the scattering angle and $\lambda$ the wavelength) measured after nickel evaporation. Shown are the measurements (symbols) and fits (solid lines) for sample I as-prepared (gray) and sample II as-prepared (black), annealed (blue) and oxidized (red) NPs, whereby the curves are scaled for clarity. The oscillations are a clear indication for the presence of the NPs. From fitting an electron density profile to the data, the thickness and coverage of the NPs are determined and these results are listed in Table 1.

![AFM image](image-url)

**Figure 1.** (left) AFM phase contrast image of the YSZ(111) surface after nickel evaporation (sample I). (middle) Height profile from the topographic data along the line as indicated (left). The typical NP height is around 3 nm. (right) 3D representation of an approximately 80 x 80 nm$^2$ area.

![XRR curve](image-url)

**Figure 2.** X-ray reflectivity vs the momentum transfer along the surface normal $Q_{\theta} = 4\pi \sin(\theta) / \lambda$, with $\theta$ half the scattering angle and $\lambda$ the wavelength) measured after nickel evaporation. Shown are the measurements (symbols) and fits (solid lines) for sample I as-prepared (gray) and sample II as-prepared (black), annealed (blue) and oxidized (red) NPs, whereby the curves are scaled for clarity. The oscillations are a clear indication for the presence of the NPs. From fitting an electron density profile to the data, the thickness and coverage of the NPs are determined and these results are listed in Table 1.

| Sample | Coverage | Height (nm) |
|--------|----------|-------------|
| Sample I | 0.15 | 3 |
| Sample II | 0.12 | 3.5 |

Table 1. Comparison of the coverage and height of the Ni NPs in the as-prepared state for samples I and II.
**Table 1. NP Average Height and Total Coverage Obtained from the X-ray Reflectivity Measurements**

| treatment | sample | h (nm) | coverage (−) |
|-----------|--------|--------|--------------|
| as-prepared | I      | 3.6    | 0.6          |
| as-prepared | II     | 3.9    | 0.7          |
| annealed | II      | 4.8    | 0.4          |
| oxidized | II      | 5.3    | −          |

“Due to coexistence of Ni and NiO, it is not possible to reliably determine a coverage and merely the total apparent thickness is determined.

**Nanoparticle Orientation.** Once the crystalline Ni NPs were grown, the positions of their Bragg peaks with respect to those of the underlying substrate were used to determine their orientation. In the following, several notations will be used interchangeably, depending on the particular frame that is referred to. Due to conventions in surface diffraction, use is made of the YSZ(111) surface unit cell to construct the reciprocal basis vectors of the substrate frame. The direct space frames related to the YSZ(111), fcc bulk Ni and Ni(111) orientations. In the following, several notations will be used those of the underlying substrate were used to determine their

| (H,K,L) Coordinates Expressed in the Different Frames Related to the YSZ(111), fcc Bulk Ni and Ni(111) Oriented Unit Cells |
|---------------------------------------------------------------|
| YSZ-111 | Ni-bul | Ni-111 |
| (−1.44,0,1.44) | (1.1,−1) | (−1,0,1) |
| (−1.44,0,2.88) | (0,0,2) | (−0,0,2) |
| (−1.02,0,3.34) | (1,1,1) | (0,0,3) |
| (−1.25,0,2.53) | (1,1,1) | |

(H,K,L) values in the different frames. By mapping out reciprocal space in selected areas, we have found two preferred NP orientations and at least one other not yet reported for the epitaxial growth of Ni NPs. The first major one corresponds to the Ni (111)-direction parallel to the substrate surface normal. The in-plane directions of the Ni lattice were found to align with the substrate surface unit cell directions. This orientational relationship (OR) is described by [001]_{YSZ}[001]_{Ni−111} and [110]_{YSZ}[110]_{Ni−111} and will be denoted OR1 in the remainder of this paper. The (1,0,2)_{Ni−111} Bragg peaks are found in a plane (H,0,L) at H=−1.44 (see Figure 3), indicating that the Ni is completely relaxed and adopts its bulk lattice parameter because this value corresponds exactly to the ratio between the bulk lattice parameters a_{YSZ}/a_{Ni}. Two peaks, which belong to [111]-oriented particles as described above, at H=−1.44 but at different L-values are seen, corresponding to the Ni-bul (11 1) and Ni-bul (002) reflections. These Ni peaks indicate that the Ni atoms follow an ABC-type stacking along the substrate surface normal. If there were only one unique stacking sequence of the Ni atoms, only one of these peaks would be visible, because the 3-fold symmetry axis of the fcc Ni along its body diagonal would be preserved. Instead, the observation of both peaks indicates that the Ni atoms have two different stackings, which results in an apparent 6-fold symmetry axis around the stacking direction, which was also evident from scanning the sample around the surface normal whereby diffraction peaks separated by 60° appeared (not shown). This diffraction feature indicates that the Ni NPs possess an internal twin structure, that different NPs possess different stacking sequences starting from the substrate, or a combination of both of these. From the peak widths along the L direction, it is concluded that internal twinning does not occur frequently because this effect would lead to additional broadening and would result in lower apparent NP heights, as explained in more detail in the section Nanoparticle Shape and Adhesion Energy.

Another strong Ni-bul (111) peak is observed at (T0,3,28), which originates from NP which are 43.3° tilted with respect to the (111)-oriented particles. This OR2 is described by [001]_{YSZ}[001]_{Ni−111} and [201]_{YSZ}[201]_{Ni−111}, where R indicates a rotation. The full 3D information is confirmed by the observation of a (2,2,0)_{Ni−bul} reflection, belonging to OR2 and which is rotated by 34.4° from the substrate surface plane. The angular position of this reflection is obtained by rotating the (0,2,2)_{Ni−bul} of OR1, which makes an angle of 30° with the plane of the RSM shown in Figure 3, around the [201]_{YSZ} direction by 43.3°. The atomic-scale arrangement, schematically depicted as a side view along the rotation axis, is shown in Figure 4. The orientation can be understood from a so-called coherent tilt strain-relieving mechanism, which is rather common in thin film heteroepitaxy. 13−15 For fcc metals, this epitaxial relationship originates from the diffusion of dislocations along (111) slip planes. 16 The resulting edge dislocations line up laterally at the hetero interface, thereby reducing the strain and tilting the metal lattice. The energetics of this mechanism competes with other types of strain relaxation 17 and can be kinetically hindered by dislocation movement. Therefore, depending on the growth technique in combination with temperature, which determines the supersaturation and surface diffusion, different orientations are expected. Nanoparticles as investigated here, would actually form the very early growth stage of textured polycrystalline thin
the reciprocal lattice units. All the experimentally reported ORs, but not on the OR2 found by our X-ray study. Interestingly, from the geometrical analysis of coincident lattice points, Sasaki et al.\textsuperscript{18} find that the best match would be formed by [010]\textsubscript{YSZ}∥[100]\textsubscript{Ni-bulk} and [001]\textsubscript{YSZ}∥[705]\textsubscript{Ni-bulk} an OR that has experimentally never been verified, also not in this study. This point illustrates that Ni-YSZ lattice-matching alone is not enough to describe the different ORs and that other energy terms such as chemical bonding and dislocation formation and their kinetic interplay during growth play a potentially more important role. Moreover, it has been shown previously that the YSZ(111) possesses a surface morphology with 2D monolayer high islands,\textsuperscript{11,22} which is expected to play a role in the NP binding.

**Nanoparticle Shape and Adhesion Energy.** The average size of the NPs can be determined from the widths of their corresponding Bragg peaks, under the assumption that the line broadening can be mostly attributed to their finite size and that nonuniform strain plays a minor role. The experimentally observed diffraction peaks are further broadened by the instrument resolution, which in the case here is anisotropic due to the synchrotron radiation characteristics in combination with the beamline focusing optics. From the single-crystal substrate Bragg peaks the in- and out-of-plane instrument resolution is determined. Because our sample coordinate system is chosen such that the HK-plane lies horizontal and the L-direction is vertical, the instrument resolution can be described by 

\[ \sigma_{\text{in-plane}} = (0.025,0.060), \]

so that the peak breadths are corrected for the instrumental resolution by

\[ \sigma = \sigma_{\text{exp}} - \sigma_{\text{res}}. \]

The average height of the NPs is given by the following reciprocal relationship:

\[ h = \frac{c}{\Delta L} \] (1)

where \( c = 0.890 \) nm is the direct lattice parameter of the YSZ(111) surface unit cell and \( \Delta L \) the peak width (fwhm) along the L-direction corrected for the instrument resolution. A similar expression holds for the determination of the average widths (\( w \)), for which the peak profile along the H-direction must be considered together with the fact that the H-direction makes an angle of 30° with the real space atomic layers within the hexagonal surface unit cell. The NP heights and widths have been determined after each of the treatments, and the resulting values are presented in Table 3. The errors that are listed are calculated from the spread in values obtained from several Bragg peaks at different positions in reciprocal space.

| orientation     | 111 | tilt |
|-----------------|-----|------|
|                 | \( h \) (nm) | \( w \) (nm) | \( h \) (nm) | \( w \) (nm) |
| as-prepared     | 4.0 ± 0.1 | 8 ± 2 | 4.6 ± 0.1 | 4 ± 2 |
| annealed        | 5.0 ± 0.2 | 8 ± 2 | 5.4 ± 0.2 | 6 ± 2 |
| oxidized        | 4.8 ± 0.2 | 9 ± 2 | 5.4 ± 0.2 | 8 ± 2 |
| NiO             | 4.2 ± 0.3 | 10 ± 2 |

In a next step, the average sizes are used together with Wulff’s construction\textsuperscript{23} to deduce the NPs’ equilibrium shape when in contact with a foreign substrate. The underlying principle is that the NPs are faceted and that those facets with the lowest surface energy will have the largest surface area. This aspect is now combined with the geometrical constraint that the nickel NPs are supported by the YSZ substrate. It is important to note that the description of the NPs’ shape used in the following is valid for isolated particles (i.e., in the absence of particle–particle interaction). From the AFM measurement, shown in Figure 1, it can be concluded that coalescence may have set in for certain particles/areas but probably not for all. A more detailed analysis is hampered by the inherent lateral resolution of the used AFM. Nevertheless, the sample used for this study is probably not far off a model system with completely isolated NPs. For fcc metals like Ni, the Wulff shape (i.e., without support) is given by a polyhedron with predominantly (111)-oriented hexagonal facets together with smaller square (100) facets. This basic shape is taken as a starting point to construct the shape when in contact with a substrate. Using the dimensions and orientation with respect to the substrate, the Wulff shape has to be cut at particular positions.\textsuperscript{24} For the (111)-oriented particles, the Wulff shape is shown in the upper part of Figure 5a. The width of 8 nm and height of 5 nm, as determined previously, require a truncation of the Wulff-shape, as shown in the lower part of Figure 5a. The resulting shape of the (111)-oriented NPs is then given by a square (111)-oriented top facet, six (111)-oriented side facets and three (100)-oriented side facets. The shape of the tilted NPs is determined by rotating the Wulff-shape by 41.3° in order to comply with the experimentally determined

![Figure 4. Schematic view of the atomic interfacial arrangement for the tilted NPs. The particular arrangement originates from an interfacial strain driven slip mechanism, which is common in fcc metals. By the diffusion of dislocations along the (111) slip planes toward the interface, the projected d-spacings have a better match with the substrate thereby relieving strain. As a consequence, the NP is tilted.](image)
Then this tilted particle is truncated at the experimentally determined height, see Figure 5b.

The energy of adhesion for relatively round supported NPs (i.e., which are not very flat and at least half as high as the Wulff-constructed free particle) is given by

\[ W_{\text{adh}} = 2y_{111} - \sqrt{\frac{3}{2}} \frac{h}{w} y_{100} \]  

(3)

This relation gives, together with \( y_{100} = 2.2 \, \text{J/m}^2 \) (see parenthetical note above), \( W_{\text{adh}} = 2.1 \, \text{J/m}^2 \). The adhesion energy value obtained from eq 2 is somewhat smaller than typical values obtained for other materials systems, such as PtRh-Al₂O₃ and Pd-Al₂O₃. The value obtained using eq 3 is much closer to those values and is in very good agreement with the value obtained for much larger (\( w = 200 \, \text{nm}, h = 150 \, \text{nm} \)) Ni particles. For the tilted NPs, a higher \( h/w \) ratio is observed, pointing to a reduced adhesion energy. The occurrence of two distinct NP growth directions can be related to a difference in interfacial binding which either could originate from a lateral chemical inhomogeneity of the YSZ substrate or a kinetically trapped state. Also a size dependence cannot be ruled out which is difficult to investigate due to the inherent size distribution of the NPs after growth via thermal deposition.

**Nanoparticle Oxidation.** At a temperature of 573 K, the NPs were exposed to molecular oxygen at a pressure of \( 10^{-3} \, \text{Pa} \) for approximately 35 min, after which the oxygen was pumped off again. Figure 6 shows a reciprocal space map after oxidation from the same plane as that shown in Figure 3. Clearly observable are two new Bragg peaks along the \( L \)-direction at \( H = -1.24 \), which originate from NiO. From the position of these two peaks with respect to the nearby Bragg peaks of the Ni \([111]\)-oriented NPs, it is concluded that the NiO has formed epitaxially on these particles. The average heights and widths of the \([111]\)-oriented and tilted NPs after oxidation are listed in Table 3. Additionally, the temporal evolution during oxidation of some structural parameters were followed as well, see Figure 7. The integrated Bragg peak intensity, which is proportional to the amount of pure metal, is seen in the decay below half of its initial value, which means that about 65% of the Ni contained by the \([111]\)-oriented NPs transforms into NiO. At the same time, the average height of the \([111]\)-oriented NPs changes only by approximately 0.2 nm, which is equal to the estimated error, see Table 3. Nevertheless, the data do indicate a trend, whereby the average height of the pure metal (core) is reduced. The particular Bragg reflection that was followed during oxidation gives an average height somewhat smaller than the value obtained from other Bragg reflections and therefore is not identical to the values listed in Table 3.
Bragg peak along $L$ can be used to determine changes in the uniform strain of the NPs’ Ni (111)-planes along the substrate surface normal. By comparing its shift from its initial value, which relates to $d_{002}$, the relative strain state $\Delta d/d_0$ is calculated. It is seen in Figure 7 that as oxidation proceeds, the lattice expands along the surface normal and levels off after an approximately 0.5% increase, a value very close to that found during thin Ni film oxidation.\textsuperscript{29} We argue that this can be attributed to oxygen incorporation into the Ni lattice. From the trend in the intensity curve, it is concluded that the oxidation process had not yet finished, although the lattice did not expand anymore, which indicates that the oxygen dissolution has reached a final state.

In order to rationalize the obtained results, we postulate the following oxidation mechanism. One important size ingredient is that small NPs oxidize relatively faster than large ones; their so-called burn-up time is even lower than expected from the oxidation rate of planar surfaces, because the geometry of the electric field around these often more-rounded particles is predicted to accelerate the oxidation process.\textsuperscript{30,31} Larger NPs will first form an oxide skin around them, and eventually, they also burn up completely, but with a much lower rate. Schematically, an intermediate state of this scenario is depicted in Figure 8a, which represents the situation after the oxidation step presented here. Given a certain particle size distribution, the resulting Bragg peak shape can be calculated by the weighted sum of the individual NP contributions. Figure 8 shows the results for such a calculation, using a hypothetical Gaussian width distribution, around an average of 8 nm and a standard deviation of $\sigma_{\text{avg}} = 3$ nm. Gaussian-shaped diffraction peaks corresponding to each of the NP size represented in the distribution are used in the calculation. A cutoff value around 5.5 nm is used, below which the nickel NPs are completely oxidized. From the resulting Ni and NiO Bragg peaks the average NP widths are determined from their breadths. It is important to note that the Ni lattice expands upon oxygen incorporation. Therefore, the width of a NiO NP, which has formed from a metal Ni particle, is larger by a factor of 1.19, which reflects the ratio of their lattice parameters. The same lattice expansion accounts for the shift of the NiO peak w.r.t. metal Ni. In this particular numerical example, the average Ni NP width before oxidation is 8 nm, whereas after oxidation, both Ni and NiO widths are 9 nm. Although this numerical simulation certainly does not include all the details of the oxidation process, it does show how the average NP sizes can in principle be affected by a preferential oxidation of small particles and how this can lead to average NP widths that are larger after oxidation. The simulation presented here does not differentiate between partially and completely oxidized particles, although the experimental results point toward such a situation. This is mostly seen in the large anisotropy between the oxidation of the NPs top 111 facet and the average widths. Both XRR and high-angle Bragg peaks indicate that upon oxidation, the average height of the metal Ni NPs is slightly reduced, at most by 0.2 nm. It has been observed that during the oxidation of a Ni(111) single-crystal surface under identical

![Figure 8](image_url)
conditions as used in this work, a NiO skin of approximately 2 nm forms after approximately 14 h. Therefore, it seems reasonable to assume that for the oxidation time investigated here, at most, only one single outermost layer of Ni atoms, which constitute the top facets, form an ultrathin nickel oxide. The oxidation process at the other facets, like 100, seems to proceed much faster and even leads to complete oxidation of nickel NPs.

The oxidation behavior of the NPs belonging to OR2 has not been followed in situ, but the overall changes in height and width, as listed in Table 3, are very similar to those of OR1. The intensity loss on the metal Ni Bragg peaks is about 50%, very similar to that of the peaks belonging to OR1. We therefore conclude that the fact that the particles belonging to OR1 have different facets exposed to the gas phase leads to minor changes in oxidation behavior and the stability of the particles is not much different.

### SUMMARY AND DISCUSSION

Nickel NPs were grown in UHV by PVD using an electron beam evaporator with a nominal average height of approximately 4 nm at substrate temperatures of 623 K. X-ray diffraction revealed that two distinct NP orientations form; there is no random orientational growth which would give rise to powderlike diffraction patterns. The NP orientations are OR1: Ni (111) planes parallel to the surface whereby the in-plane directions are also aligned (Ni[111])||YSZ[111] and Ni[1 1 0]||YSZ[1 1 0]) and OR2: Ni 111 planes tilted by 41.33° from the substrate normal in the plane spanned by YSZ[111] and YSZ[1 1 0]. The average heights and widths of the NPs were determined from the X-ray diffraction line breadths. The relatively well-defined height is furthermore extracted from X-ray reflectivity and AFM in a separate growth run, which all give systematically comparable values.

Sintering is observed after annealing the NPs to 923 K in UHV. The average heights and width of NPs in both ORs increase by approximately 25%, indicating that the particles exhibited already equilibrium shape at the growth temperature. From the height-to-width (h-to-w) ratio, together with the Ni (111) and (100) surface energies, the adhesion energy is determined. Depending on the NP shape being more round or flat, two different relations hold. Because the NPs’ average aspect ratio $h/w$ is close to $3/4$, either of the relationships might give representative values. This is even more likely when taking into account the appreciable size distribution, which is more broad in $w$ than in $h$. The more rounded NPs will then have an adhesion energy of 1.4 J/m$^2$ and the flatter ones 2.2 J/m$^2$. The more stable, flat NPs’ adhesion energy compares rather well with literature. This adhesion energy calculation does not hold for the tilted NPs forming OR2 because of their asymmetric shape.

When exposing the NPs to methane at a pressure of $10^{-3}$ Pa and a temperature of 573 K for 30 min, no changes are observed. A possible adsorption of the hydrocarbons on the NPs’ facets is thus concluded not to affect the structure of the NPs. The most distinct changes are caused by an oxygen treatment at $10^{-3}$ Pa and 573 K for 35 min. The intensity of the OR1 Bragg reflections, which is a measure for the total amount of metal, decreases to less than half its initial value. After the oxidation step, NiO Bragg reflections are detected, and from their positions in reciprocal space, it is deduced that NiO has grown epitaxially, in a cube-on-cube fashion, on the NPs from OR1 or in contact with the YSZ (111) surface. At the same time, the average height has changed by $-0.2 \pm 0.3$ nm and the average width $+1 \pm 3$ nm. The average size of the NiO is approximately equal to that of the remaining pure metal particles. These results can be rationalized by considering a preferential oxidation mechanism in combination with an anisotropic size distribution, whereby the spread in h is much narrower than that in w. It has been predicted that small, more rounded, NPs will oxidize at an enhanced rate compared to larger ones. On the basis of these and our experimental results, we postulate that Ni NPs smaller than approximately 5.5 nm have burnt up completely and that larger ones have a NiO skin formed around them. A simulation, using a hypothetical Gaussian width distribution, shows that indeed this scenario can explain the experimentally observed average widths before and after oxidation. This description does not include all the details of the oxidation process, such as exact oxidation rate and NiO thickness on the different facets, and even assumes that part of the larger NPs does not oxidize at all, which is not very realistic. Nevertheless, it shows numerically the effect one important aspect of the mechanism, namely, size-dependence, can have on the final average size. The size-dependent oxidation behavior might also be related to the kink seen after approximately 3 min in the time-dependent intensity reduction of the 111 Bragg peak of Figure 7.

The average size of the NiO particles and/or skin is of the same order of magnitude as the remaining pure Ni metal (cores) because of two effects: (1) Due to the lattice expansion after oxidation (i.e., NiO has larger lattice constants than Ni), a completely oxidized NP will be larger than the original one. This effect shifts the average oxidized NP size to higher values, thereby compensating for the fact that the smaller metal particles have prefentially oxidized. (2) The oxide skin on the top facet is formed by a completely structurally correlated NiO lattice. Therefore, the in-plane NiO size will be comparable to the underlying metal particle. From Ni(111) single-crystal oxidation studies, it was found that an approximately 2 nm oxide forms after 14 h at conditions similar to the ones here. Extrapolating to the oxidation time used here, it would be expected to have oxidized only a monolayer from the 111 facets, which is about 0.2 nm thin. This value corresponds very well to the reduction in the average height of the (111)-oriented NPs upon oxidation and would imply that the oxidation proceeds mostly along the (100) facets.

The results obtained here can be discussed in relation to real SOFCs, in particular with respect to the so-called redox cycling (i.e., the oxidation—reduction process of Ni). During SOFC operation, the anode is continuously supplied with fuel, the amount of which is burnt depends on the availability of oxygen. Instabilities around the ideal ratio of fuel and oxygen levels can lead to the formation of NiO, which is known to lower the SOFC performance and lifetime by stress development, lowering of the metal triple phase boundary density, and mechanical failure.

Our results may add another cause to SOFC anode failure, namely, that during the time when there exists a surplus of oxygen, probably the smallest Ni NPs will completely oxidize and, depending on the reducing properties of the fuel, might not revert to pure metal anymore. After many cycles of such a process, the SOFC might gradually lose its efficiency because the smallest particles are most likely to be the most reactive and therefore relatively more important for the functionality. Moreover, such a preferential oxidation process, whereby the particle size distribution shifts toward larger values,
might result in the SOFC operation to drift away from complete reaction leaving unburnt fuel and increasing oxygen levels thereby oxidizing ever more Ni.

**CONCLUSIONS**

X-ray diffraction revealed two distinct orientations of Ni nanoparticles grown in UHV by MBE: [111]-oriented particles and ones with their [111] planes tilted by 41.33° from the surface normal. A combination of diffraction line width analysis, X-ray reflectivity, and AFM delivered information on the average NP height and width. These sizes were used to determine the energy of adhesion to be in the range of 1.4−2.2 Jm−2, whereby particles that have a more round shape are more weakly bound than those that have a flatter geometry. Annealing the NPs in UHV to 923 K led to the observation of sintering: most significantly, their average height increased and the data also indicate an increase in average width. This sintering process does not lead to a significant shape change from just after growth. Exposure to methane at 10−3 Pa at a temperature of 573 K did not show any structural changes. However, oxidation at 10−3 Pa of O2 at the same temperature led to the formation of expitaxial NiO on the [111]-oriented particles. An oxidation mechanism is postulated, which is based on a preferentially faster burn up rate for small particles and the formation of an oxide skin around larger ones. Such a preferential oxidation mechanism which shifts the NP size distribution toward higher values might be one factor responsible for the long-term degradation of SOFCs.

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**Notes**

The authors declare no competing financial interest.

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