In situ x-ray study of the oxidation of a vicinal NiAl(6,7,1) surface

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New Journal of Physics 11 (2009) 113004 (15pp)
Received 10 August 2009
Published 4 November 2009
Online at http://www.njp.org/
doi:10.1088/1367-2630/11/11/113004

Abstract. We present an in situ surface x-ray diffraction study of the clean, oxidized and subsequently annealed surfaces of regularly stepped NiAl(6,7,1). Our results show that the UHV stable, clean surface is not faceted and consists of a regular array of (1,1,0) terraces and (0,1,1) steps. The topmost Al and Ni atoms on the terraces exhibit a rippled relaxation while the step atoms are relaxed towards the bulk. Preferential Al oxidation at 540 K and $6 \times 10^{-6}$ mbar $O_2$ leads to the formation of a 5 Å thin, disordered alumina layer and induces Al vacancies and Ni anti-sites in the Al-depleted interfacial region. The terrace-step structure of the clean surface is maintained, but strong inward relaxations of the interfacial atoms change the strain field around the steps. Massive (1,1,0) faceting with facets up to 50 times larger than the original terraces occurs after high-temperature annealing, during which the surface oxide develops a complex long-range ordering. These results can be understood by the change of interfacial strain, which removes the energy barrier for mass transport. In addition, unlike in the case of low-index (1,1,0) surfaces, we find the step-induced suppression of twin domain formation in the alumina film grown on NiAl(6,7,1). Our results show that the interplay between oxidation and strain can have dramatic effects on the morphology of vicinal surfaces.

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1. Introduction

Ultrathin oxide layers on metal and alloy surfaces are often used as nanotemplates for growth and catalytic studies of nanoparticles but may also become interesting as insulating barriers in microelectronic devices [1]–[3]. One nanotemplate often used as stable support for active metal particles is the ultrathin, well-ordered surface oxide grown on NiAl(1,1,0) [4]–[6]. The epitaxial, flat Al$_2$O$_{3-\delta}$ film can be prepared with high reproducibility and smoothness. It possesses a complex, double-layered atomic structure forming defects like twin- and anti-phase domains [7]–[11]. These defects act as nucleation sites for the particle growth but also provide an unwanted contact to the metal substrate. Therefore a large, single-domain, defect-free surface oxide film would be desirable for the mentioned applications.

One approach to tailor the oxide growth on a surface is by using vicinal surfaces with oriented step edges [12]. Steps and kinks are present on all surfaces of single crystals, nanoparticles and polycrystalline materials. Due to their lower coordination number compared to bulk and on-terrace surface atoms, step atoms play an important role in surface processes such as oxidation, catalysis and epitaxial growth. They act as preferential adsorption sites and nuclei for the initial formation of oxides, are favourable pathways in inter- and intralayer diffusion processes and have an important role for the release of interfacial strain, set up during oxide formation [13]–[16].

To gain a detailed understanding of the structural changes at steps during oxidation and catalytic reactions, regularly stepped surfaces are investigated as model systems. Studies of regularly stepped surfaces also offer a convenient way to expand our knowledge from low-index single crystals toward polycrystalline materials and nanoparticles.

Most of the previous studies on vicinal surfaces have focused on pure metals like Pt, Rh or Pd. By combining several experimental and theoretical techniques, complex faceting behaviour as well as the formation of different surface oxide phases could be observed during oxygen exposure of Rh(5,5,3) and Pd(5,5,3) [15, 17, 18]. By combining surface x-ray diffraction (SXRD) with density functional theory (DFT) or molecular dynamics (MD), the atomic structures of clean Pt(9,7,7), oxidized Cu(4,1,0) and Cu(1,1,5) were studied [19]–[21].
Very little investigations exist on vicinal surfaces of binary alloys within the context of surface oxide formation. A recent STM study of NiAl(14,16,1) shows that during oxidation the initial sequence of identical (1,1,0) terraces is lifted in favour of large facets and that presence of surface steps induces the formation of a single-domain oxide [12].

In this work, we report on changes of the surface structure and the near-surface chemical composition during the oxidation and annealing of a NiAl(6,7,1) surface, using SXRD and low-energy electron diffraction (LEED). We show that the clean, nearly bulk-like surface is characterized by a regular pattern of 14 Å wide (1,1,0) terraces and monoatomic (0,1,1) steps. Al and Ni atoms in topmost terraces exhibit a rippled relaxation. The terrace-step structure of the clean surface persists at the oxide–alloy interface after oxidation at 540 K and $6 \times 10^{-6}$ mbar $O_2$ while the atoms of the interfacial region are relaxed inwards. A 5.5 Å thick, disordered alumina film is formed. Oxidation induced formation of Al and Ni vacancies as well as Ni anti-sites at the interface is observed up to a depth of 1 nm. We demonstrate that high temperature annealing enables long-range ordering of the oxide, inducing (1,1,0) facets up to 50 times larger than the original terraces. The surface oxide with its complex structure is known from the oxidation of NiAl(1,1,0) but due to the surface steps a suppression of twin domain formation is observed on NiAl(6,7,1).

In the following paragraph the NiAl(6,7,1) system is introduced, SXRD from the vicinal (6,7,1) surface is discussed briefly and details of the experiment are given. In sections 3 and 4, the results of the clean, oxidized and annealed sample are presented and discussed, while final conclusions are drawn in the last section.

2. Experimental details

A single crystal of nominal composition Ni$_{50}$Al$_{50}$ was grown, cut and polished in-house at the Max Planck Institute for Metals Research in Stuttgart, Germany. The (6,7,1) surface orientation was confirmed by LEED and x-ray diffraction (XRD) measurements. The sample was mounted in a portable, ultrahigh vacuum (UHV) in situ oxidation chamber allowing for temperatures from room temperature up to 1700 K, and gas pressures from $10^{-10}$ up to $10^{-4}$ mbar. Following the standard procedure for obtaining a clean NiAl(1,1,0) surface, the sample was prepared by several cycles of Ar$^+$ ion sputtering and annealing to 1300 K, including annealing in an oxygen atmosphere to remove carbon [9]. Auger electron spectroscopy was used to check for surface contaminations. The contamination free sample surface was oxidized at 540 K and $6 \times 10^{-6}$ mbar $O_2$ for 900 s. To obtain a long-range ordered surface oxide the sample was annealed at different temperatures between 620 and 1190 K. The SXRD experiments were carried out with a photon energy of 15 keV at beamline ID03 of the European synchrotron radiation facility (ESRF) in Grenoble, France [22].

The structure of the bulk terminated NiAl(6,7,1) surface is depicted in figure 1, together with an out-of-plane side view of its corresponding reciprocal space. The [6,7,1]-direction makes an angle of 7.6° with respect to the [1,1,0]-direction. The surface consists of a seven atomic rows wide (1,1,0) terraces (14 Å) with mono-atomic (0,1,1) steps. The real space surface unit cell is defined by the orthogonal vectors $(a_1, a_2, a_3)$, where $a_1$ runs along the steps in the $[\bar{1}, 1, \bar{1}]$-direction of bulk bcc NiAl, $a_2$ across the steps in the $[8, 5, 13]$-direction and $a_3$ defines the $[6, 7, 1]$ surface normal. No ragged shape of the step edges is expected as the $a_1$, direction points along a low-energy step orientation on the (1,1,0) surface [12]. The corresponding
The NiAl(6,7,1) unit cell consists of an orthorhombic unit cell containing 258 Ni (blue) and 258 Al (yellow) atoms. The red rectangle marks the surface unit cell of the (1,1,0) surface.

**Figure 1.** (a) Three-dimensional (3D) view of the bulk-terminated NiAl(6,7,1) surface: thin black lines mark the orthorhombic unit cell \( (a_1 = 5.00 \, \text{Å}, \quad a_2 = 46.37 \, \text{Å}, \quad a_3 = 26.77 \, \text{Å}) \), containing 258 Ni (blue) and 258 Al (yellow) atoms, respectively. The red rectangle marks the surface unit cell of the (1,1,0) surface. (b) Side and top view of the system: one quasi-row \( R \) consists of seven layers perpendicular to the surface normal. (c) \((K,L)\) reciprocal space plane of the (6,7,1) surface for \( H = 0 \), together with a sketch of the steps for better orientation. Thick black lines show the CTRs running through the Bragg peaks (black circles) perpendicular to the surface. For even \( H \) coordinates the CTRs arise from the fundamental bcc lattice, for odd ones from the CsCl superlattice.

The atomic density of high Miller index vicinal surface planes is reduced in comparison to low index surfaces. This strongly decreases the intensity along the CTRs of vicinal surfaces. The intensity at the anti-Bragg point is reduced by more than two orders of magnitude compared with the low index (1,1,0) surface. These features complicate CTR measurements of vicinal surfaces and make a small surface roughness (here: below 2 Å) and a high photon flux (here: \( 10^{13} \, \text{ph} \, \text{s}^{-1} \) focused on \( 50 \times 30 \, \mu\text{m}^2 \)) necessary for the experiment. The SXRD measurements were carried out with a fixed incidence angle close to the critical angle of NiAl at 15 keV \( (\alpha_c = 0.19^\circ \text{at} \, 15 \, \text{KeV}) \). The CTR data were obtained by taking rocking scans at each point along the CTR, followed by an integration and applying standard corrections \[24\]. Two fundamental and two superstructure CTRs were measured, resulting in 197 independent structure factors. In absence of redundancy of the data, the average error was set to 10%, which is a typical value using this setup. To analyse the data, the program ROD was used to compare different structure models to the experimental structure factors \[25\].
Figure 2. Two fundamental (A2 type) and two superstructure (B2 type) CTRs were measured for the clean (red squares) and oxidized, but not annealed surface (black circles), respectively. The results of the best fitting, structural models are shown by solid lines, the dashed lines show the fitting result from bulk-terminated models. The two data sets are shifted for clarity.

3. Results

3.1. Atomic structure of the clean surface

To obtain a detailed picture of the terrace and step structure on the atomic scale, CTR measurements of the clean sample were performed. The experimental structure factors are shown in figure 2. As described in the previous section, the signal on the CTRs is very low for vicinal surfaces. Therefore only parts of the CTRs in the vicinity of Bragg peaks were measurable in the present experiment. Another factor hampering the quantitative description of a vicinal surface is the large number of parameters needed to describe the structural relaxations. In principle, every layer within the surface region relaxes in a different way. As the out-of-plane layer spacing of 0.31 Å of the (6,7,1) planes is very small, many layers will be affected by the presence of the surface. For NiAl(1,1,0) it is known that within the first two layers up to a depth of about 4 Å Al and Ni are relaxed out- and inwards, respectively [26, 27]. Assuming relaxations up to a similar depth for the (6,7,1) surface, relaxations of the first 14 layers are expected. In addition, the atoms may relax not only along surface normal \( \mathbf{a}_3 \)- but also along the \( \mathbf{a}_2 \)-direction due to the existence of the undercoordinated step atoms. As the experimental data set is not large enough to include all relaxations described above, we used a simplified model to analyse the data.

The parameters of this structural model are depicted in the side view of figure 1(b). The red lines, labelled R1, mark all atoms sitting in the top most (1,1,0) terraces of the (6,7,1) surface. All these atoms are allowed to relax along the \( \mathbf{a}_1 \)-directions element specifically. The blue and red lines (R2 and R3) mark the atoms within the buried second and third topmost ‘quasi’ rows of (1,1,0) terraces, respectively. According to DFT and MD calculations of other vicinal surfaces [19, 20], [28]–[31], the step and corner atoms are relaxed in a more pronounced way compared with the terrace atoms with strong relaxations not only along the surface normal but also across the steps (\( \mathbf{a}_2 \)-direction). Therefore the atoms labelled S1, C1, S2 and C2 in
Figure 3. Schematic side views of the relaxation profiles of the clean (a) and oxidized (b) samples, resulting from the CTR fits. The relaxations of the Al and Ni atoms are presented by blue and red arrows, respectively. The arrows are magnified by a factor of 5. Black dots show the bulk positions, the grey dotted lines represent the bulk-terminated step. Parts (c) and (d) depict the row-dependent (R1, R2, ...) occupancy profile for Ni, Al and Ni anti-sites for the oxidized surface region. ‘Quasi’-row 1 is at the oxide–alloy interface. The sketched bulk unit cells illustrate the ordering and defects in the bcc lattice.

Figure 1(b) are allowed to relax in the $a_2$- and $a_3$-directions. Ni and Al atoms are allowed to relax independently for all positions. In addition a terrace width distribution is included into the fitting model by applying the so-called beta model [32]. It models the surface coverage per layer $n$ by a power law ($\beta^n$, with $0 < \beta < 1$) and is usually used to describe surface roughness. In total 21 structural parameters and one scaling parameter are needed for the simplified model.

The best fit using the above model is shown by the red line in figure 2. The corresponding real-space model and the fitting values are presented in figure 3(a) and table 1. The normalized residue of the best fit is $\chi^2 = 1.4$. The result shows a 0.23 and 0.12 Å rumpling of Ni and Al within the first and second row (R1 and R2 in figure 1(b)), respectively. Al atoms relax outwards, Ni inwards. Relaxations within the third row R3 were not observed. The Al and Ni atoms at the step (position S1) are relaxed towards the step edge, while the corner atoms (position C1) are both relaxed outwards. The step atoms of the second row (positions S2) exhibit a more pronounced rumpling compared with the corresponding terrace atoms of row R2. The corner atoms of the second row (position C2) are slightly relaxed towards the corner of the kink. As seen in table 1 the error bars for the relaxations of the individual step and corner atoms are very

$$\chi^2 = \frac{1}{N-P-1} \sum \frac{(|F_{\text{exp}}| - |F_{\text{cal}}|)^2}{\sigma_{\text{exp}}^2},$$

where $N$ is the number of data points, $P$ the number of fitting parameters, $F_{\text{exp}}$ the experimental structure factor (with error bar $\sigma_{\text{exp}}$) and $F_{\text{cal}}$ the calculated structure factor.
Table 1. Results of the structural refinement of the clean and oxidized surfaces. Listed are the displacements \( \Delta z \) along the surface normal and \( \Delta y \) in the direction across the steps for each atom in the rows R1 to R6 as well as at the steps and corners (S1, C1, S2 and C2). All displacements from the bulk positions are given in Å. The roughness parameter \( \beta \) is \((1.1 \pm 0.8) \text{ Å} \) and \((0.7 \pm 0.7) \text{ Å} \) for the clean and oxidized surfaces, respectively.

| El./Pos. | \( \Delta z (-) \) | \( \Delta y (-) \) | \( \Delta z (-) \) | \( \Delta y (-) \) |
|----------|------------------|------------------|------------------|------------------|
| Al/R1    | 0.08(9)          | 0.01(2)          | -0.4(2)          | -0.05(3)         |
| Ni/R1    | -0.15(2)         | -0.018(5)        | -0.29(6)         | -0.04(1)         |
| Al/R2    | 0.08(9)          | 0.01(2)          | -0.40(7)         | -0.05(1)         |
| Ni/R2    | -0.04(2)         | -0.005(5)        | -0.29(3)         | -0.036(6)        |
| Al/R3    |                  |                  | -0.4(2)          | -0.05(4)         |
| Ni/R3    |                  |                  | -0.22(2)         | -0.027(5)        |
| Al/R4    |                  |                  | 0.3(1)           | 0.03(2)          |
| Ni/R4    |                  |                  | 0.03(2)          | 0.004(5)         |
| Al/R5    |                  |                  | 0.25(7)          | 0.03(2)          |
| Ni/R5    |                  |                  | 0.03(2)          | 0.004(5)         |
| Al/R6    |                  |                  | 0.09(6)          | 0.01(1)          |
| Ni/R6    |                  |                  | 0.00(2)          | 0.000(5)         |
| Al/S1    | -0.1(7)          | -0.2(9)          | 0.2(7)           | 0.2(9)           |
| Ni/S1    | -0.2(1)          | -0.3(3)          | -0.2(1)          | -0.5(3)          |
| Al/C1    | 0.4(4)           | 0.0(6)           | -0.4(4)          | 0.5(6)           |
| Ni/C1    | -0.0(2)          | 0.0(3)           | -0.4(2)          | -0.5(3)          |
| Al/S2    | 0.4(2)           | -0.3(7)          | -0.4(2)          | 0.5(7)           |
| Ni/S2    | -0.3(2)          | 0.3(3)           | -0.4(2)          | -0.5(3)          |
| Al/C2    | 0.0(4)           | 0.1(8)           | -0.3(4)          | 0.5(8)           |
| Ni/C2    | -0.1(1)          | 0.1(2)           | -0.4(1)          | -0.5(2)          |

high, especially for Al with its lower electron number as compared with Ni. The errors were determined by allowing a \( \chi^2 \) increase of 10\% while fits were performed with all parameters free, except the one chosen for error estimation [25]. The large errors for the step and corner atom relaxations result from lack of data towards the CTR’s anti-Bragg positions, which are most sensitive for these relaxations.

In addition to the best-fitting structural model described above, the influence of several other parameters was investigated systematically to further confirm the findings. The investigation showed the need of the distinctive relaxations of the step and corner atoms (S1, S2, C1 and C2) for a good agreement of fit and data. Fitting of the static Debye–Waller factor of the undercoordinated surface atoms did not improve the residue.

3.2. Atomic structure after oxidation

X-ray reflectivity measurements (not shown here) after the oxidation at 540 K and 6 \times 10^{-6} \text{ mbar} O_2 show the presence of a 5.5 Å thick oxide layer, which is in good agreement with the oxide thickness found on NiAl(1,1,0) oxidized under the same conditions [8]. This layer possesses no long-range order, since no new diffraction pattern could be detected by SXRD and
LEED. The CTRs arising from the (6,7,1) surface are still present. Thus, the regularly stepped pattern of terraces and steps, observed for the clean surface, is surprisingly conserved at the oxide–alloy interface. To characterize the morphology and oxidation induced segregation profile of the interfacial region, four CTRs of the oxidized, but not yet annealed surface were measured, as shown as in figure 2. Compared with the CTRs of the clean sample, clear oscillations are visible inline with a disturbed chemical composition in the near-surface region [26]. The defects and distortions occur up to a well-defined depth, which results in by characteristic oscillations on the CTRs. Therefore the structural model described in section 3.1 was extended for the analysis of the oxidized NiAl(6,7,1) surface. Atomic relaxations as well as Ni and Al vacancies and Ni anti-sites were allowed within the first six rows (R1 to R6, see figure 1(b)).

The best fit result ($\chi^2 = 3.9$, 48 parameters) is shown in figure 2. The corresponding relaxations are given in table 1 and schematically depicted in figure 3(b). A strong inward relaxation of Ni and Al atoms is found in the first three rows (R1 to R3, see figure 1(b)), with minor relaxations in the following three rows. Comparing the two superstructure CTRs an asymmetry is visible. For the (1,5) rod the oscillation minimum is observed for lower $L$ values compared with the Bragg peak position, for the (1,8) rod for higher $L$ values. To reproduce this asymmetry, relaxations in the $a_2$-direction have to be allowed within the structure model for the step and corner atoms (S1, S2, C1 and C2). Atoms on these positions are strongly relaxed towards the bulk similar to the corresponding terrace atoms, while the inplane relaxation is different for the two constituents. Step rippling occurs where Ni atoms are shifted inplane towards the upper terrace, Al atoms towards the lower terrace.

The occupation profiles for the Ni and Al sites resulting from the best fit are shown in figures 3(c) and (d), respectively. As seen within figure 3(c), only 44 ± 6% of Ni sites are occupied by Ni within the first row at the oxide–alloy interface. Within the second row already 85 ± 5% of the Ni sites are occupied while this value smoothly increases towards the bulk value within the following rows. The occupancy profile of the Al sites, depicted in figure 3(d), shows the oxidation-induced decrease of Al concentration within the first six rows of the alloy(1.3 nm). In the first and second row towards the oxide–alloy interface Al sites are occupied with Al by 57 ± 14 and 99 ± 12%, respectively, whereas the Al occupancy drops down to 23 ± 10% in the third row. This is accompanied by the formation of Ni anti-site atoms (Ni on Al sites). From the fourth row onwards the amount of Al on Al sites start to increase towards the bulk value, whereas the Ni anti-sites are disappearing again.

As for the clean surface, the influence of the several parameters on the quality of the fit was examined by applying different structure models. In all tested models the occupancy profile was allowed to vary, but all resulting profiles were similar to the presented one. Again, the agreement factor could be strongly improved by allowing the step and corner atoms to relax independently of the terrace atoms. Introducing static Debye–Waller factors for the interfacial Ni and Al atoms did not improve the fitting results.

Finally, we note that the modulation of the structure factor of the B2 type (1,5) CTR disappeared during annealing at a temperature of around 730 K (not shown here). This indicates that the interfacial defects annihilate during annealing.

3.3. Structural changes during annealing

It is known from NiAl(1,1,0) that a long-range ordered surface oxide is formed by annealing the oxidized surface [9]. In order to follow a possible ordering of the oxide on the (6,7,1) surface,
the sample is annealed stepwise after its oxidation. Morphology changes at the oxide–alloy interface are followed by SXRD measurements. To detect a faceting of the surface, scans across the (1,5)-CTR were performed in the \(a_2\)-direction across the steps, as shown in figure 4(a). The CTR signal at \(K = 5\) starts to decrease at temperatures of 840 K while simultaneously a broad signal arises at \(K \approx 5.7\). The position of the new signal can be ascribed to the formation of (1,1,0) facets with nominal position of \(K = 5.69\). The full width half maximum (FWHM) value of the arising peak is decreasing with increasing temperatures. This corresponds to an increase of the average facet width from 9 to 17 to 71 nm at 1120, 1150 and 1190 K, respectively. Figure 4(b) shows the integrated intensity of a rocking scan, performed at the (0,4) inplane position of one surface oxide domain for different temperatures\(^3\). At 730 K a signal is detected, corresponding to the beginning of the transformation from a short-range ordered to a long-range ordered oxide. Increasing the temperature to 840 and 1120 K leads to a further increase of the signal as more long-range ordered oxide is formed. The oxide starts to desorb at 1150 K, as the signal has decreased compared with 1120 K. No new peaks are observed in the H-scans along the steps as no faceting occurs in this direction. Flashing the sample up to 1300 K reproduces the clean, regularly stepped (6,7,1) surface with no larger (1,1,0) facets.

### 3.4. Microstructure of the oxide

After annealing the oxidized sample to 1120 K for 240 s, LEED images were taken at room temperature and compared with the LEED pattern from the NiAl(1,1,0) surface prepared under the same conditions. As known from the literature, twin domain formation is observed for the surface oxide on the (1,1,0) surface \([9]\). The twin domains are rotated by +24° and −24° with respect to the \([\bar{1}, 1, 0]_{\text{bulk}}\)-direction and are labelled ‘green’ and ‘red’, respectively (see also figure 5(d)). The LEED image of the low-index surface, presented in figure 5(b), shows reflections of both domains appearing with equal intensities. In the case of the vicinal surface,

\(^3\) Lattice parameters of the surface oxide: \(a = 18.01\ \text{Å}, b = 10.59\ \text{Å}, \gamma = 91.15°\) and \(\xi(a, [\bar{1}, 1, 0]) = 24.01°\).
Figure 5. Figure (a) and (b) are LEED images of the oxidized and annealed (6,7,1) and (1,1,0) surface, respectively. The black arrows mark bulk directions of the (1,1,0) NiAl surface. The green and red arrows show the reciprocal space unit cell of the two twin domains of the surface oxide. The insets highlight the more intense reflection of the ‘red’ twin domain in case of the (6,7,1) surface showing preferential domain growth. In figure (c) the x-ray rocking scans at the positions of the two twin domains confirm the single domain growth on NiAl(6,7,1). Figure (d) shows a schematic top view of the vicinal surface and the two possible twin domain unit cell orientations. The grey grids inside the oxide unit cells mark the penta–heptagon pairs of interfacial Al atoms. The yellow lines highlight dense, ‘quasi’ rows of these Al ions.

reflections from the ‘red’ domain are much more intense than from the ‘green’ one, as seen in the LEED image in figure 5(a). The suppression of one of the twin domains was also observed during the SXRD measurements. In figure 5(c) the corresponding rocking scans, recorded for each twin domain at the same oxide peak position (marked in the LEED image by a red and green circle), show a much stronger signal for the red domain. Therefore the experimental results demonstrate the preferential oxide growth of the ‘red’ domain on the NiAl(6,7,1) surface.

4. Discussion

4.1. The clean surface

The CTR measurements of the clean sample show that the regularly stepped NiAl(6,7,1) surface is stable at room temperature under UHV conditions. It is also observed at 1190 K as the CTRs of NiAl(6,7,1) reappear after desorbing the oxide from the surface. No faceting of the clean surface is observed between room temperature and 1190 K. Thus, we conclude
that the investigated regularly stepped surface is thermodynamically stable in the investigated temperature and pressure range. The stability of clean vicinal surfaces against faceting is due to a step–step repulsion arising from the interaction of strain fields, present around every step. Capillary forces acting at the upper and lower sides of a step create an elastic force dipole at the step. These dipoles are compensated by internal strain, which is crucial for the stability on which temperature has only a little effect [33, 34].

The results from the CTR measurements show a buckling of the Ni and Al atoms within the first two rows R1 and R2. The direction and the magnitude agree, within the error bars, with the buckling of around 0.2 and 0.04 Å found for NiAl(1,1,0) [26, 27]. This good agreement is reasonable as the relaxations of the central atoms of the relatively large, seven atomic chains wide (1,1,0) terraces are only weakly affected by the occurrence of steps. The pronounced inward relaxation of Ni and Al at the step edge position S1, together with an outward relaxation of the atoms at the corner position C1 are characteristic for a surface step, as they arise from capillary forces acting at the surface on both sides across the step pulling atoms at the step inwards and at the corner outwards [34]. This leads to a rounding of the electron density at the steps, which is predicted by the theory of charge smoothing on surfaces and surface steps [35]. Similar relaxations of step and corner atoms are also found for Pt(9,7,7) in a combined MD and SXRD study or for Cu(1,1,5) in a DFT study [19, 20], [28]–[30]. In one of few theoretical studies on vicinal binary alloy surfaces, L12-structured Cu3Au(5,1,1) is investigated by DFT calculations [31]. The Cu3Au(5,1,1) surface consists of three atomic chains wide (1,0,0) terraces, alternately composed of pure Cu and mixed Cu–Au chains with a buckling of Cu and Au within the mixed chains. The characteristic inward relaxation of step atoms and an outwards relaxations of the corner atoms is also reported. The study shows that buckling of the surface atoms which is found for many low-index surfaces of binary alloys can also be observed on vicinal surfaces. This finding is confirmed by our results on the NiAl(6,7,1) surface.

4.2. Oxidation of the surface

At 540 K and 6 × 10⁻⁶ mbar O₂ a vitreous alumina film is formed which possesses short-range but no long-range order. The formation of the Al₂O₃ layer does not remove the initial sequence of identical (1,1,0) terraces as shown by the CTR measurements (see also figure 6(a)). Features such as the oxide thickness, the Ni-, Al- and Ni anti-site-occupation profile and the relaxation profile observed for the surface region of the oxidized NiAl (6,7,1) surface are very similar to NiAl(1,1,0) [36]. On both surfaces the oxide film is about 5 Å thick [8]. Strong inward relaxations of atoms especially within the first three rows are found for both surfaces. The step and corner atoms within the first two rows are also strongly shifted towards the bulk. As shown in the occupancy profiles (figures 3(c) and (d)), Al vacancies reach up to a depth of 13 Å in the alloy and originate from preferential Al oxidation during the formation of the alumina film. Thereby the amount of Al missing in the alloy matches the amount of Al needed to form the two-layer thin surface oxide known from NiAl(1,1,0) [7, 8]. At depths larger than 13 Å in the alloy the Ni sites are fully occupied. The Ni vacancies appear only very close to the oxide–alloy interface, which could also be interpreted as roughness. At a depth of around 5 Å only 23% of the Al sites are occupied by Al. As known from the NiAl bulk, an enhancement of the Ni concentration leads to the formation of Ni anti-sites (Ni on Al sites) [37]. This effect is also found here at the depth of 5 Å. During the oxidation of the Fe₃Al(110) surface at very similar conditions preferential Al oxidation is reported as well, going along with Fe anti-site formation.
Figure 6. (a) and (b) show schematic top and side views of the oxidized sample at two different annealing steps, illustrating the faceting process. Between 540 and 620 K the regularly stepped (6,7,1) surface is covered by disordered oxide, which at higher temperatures of 1120 K is transformed into long-range ordered alumina, which induces the formation of large (1,1,0) facets.

at the interface [38]. We presume that the anti-site formation of the more noble constituent (Ni, Fe, Ti) is found during the oxidation of all aluminides. The relative increase of the Ni concentration due to preferential Al oxidation could also explain the aforementioned inward relaxation of the atoms within the surface region. For bulk NiAl it is known that the lattice constant decreases by 4% if the Ni concentration is increased from 50 up to 54% due to Al vacancies [39]. Interestingly, the Al concentration directly at the interface within the first two rows is larger than in the deeper embedded third and forth rows.

Oxygen-induced surface faceting and step bunching are found during the annealing of the oxidized NiAl(6,7,1) surface. Faceting during oxide formation was observed previously for other systems like Rh(5,5,3) or Pd(5,5,3) and for the regularly stepped NiAl(14,16,1) surface [12, 15, 17]. In this work, we could demonstrate that after oxidation, the kinetic barriers for faceting are removed at temperatures above 840 K. At these high-temperature material transport is possible; both the substrate as well as the oxide undergo drastic structural changes where the former becomes faceted and the latter develops long-range order. As depicted in the upper part of figure 6(a), the oxidized, but not annealed NiAl(6,7,1) surface can be schematically described by a regularly stepped interface covered by a disordered alumina film. As shown above, oxidation induces strong changes of the relaxation pattern within surface region, especially at the surface steps. The strain field around the steps is changed. We argue that these changes lower the strain-induced step–step interactions responsible for the stability of the clean surface. However, the regularly stepped structure is still maintained due to kinetic barriers. Annealing the sample provides the necessary energy and atom mobility for structural changes within the oxide, but also for material transport from the interface to the bulk. During the ordering of the oxide, the strain is also changed, because the oxide exerts a force on the substrate. At temperatures around 730 K this induces the transformation from short-range to small amounts of long-range ordered oxide on the regularly stepped terraces while kinetic barriers are still too high for faceting. The crystallization process is believed to start at the
surface steps. Strain, set up between the ordered oxide and the alloy, is released preferentially along the steps, thereby lowering the barriers for surface oxide formation directly at the steps. This idea is supported by STM images of oxidized NiAl(14,16,1), taken after annealing up to 1000 K. They show the steps acting as nuclei for surface oxide formation [12]. At a temperature of 1120 K kinetic barriers for material transport are overcome and as more short-range-ordered oxide is transformed to long-range-ordered oxide, the regularly stepped (1,1,0) terraces are lifted in favour of large (1,1,0) facets covered by long-range-ordered alumina (see figure 6(b)). At 1150 K oxide starts first to desorb from smaller facets, which adopt the regular pattern of the clean (6,7,1) surface again. Only large facets remain, covered by long-range-ordered oxide, explaining the sharp peak found in the corresponding K-scan. Further annealing promotes this process until all oxide is desorbed. We conclude that the occurring (1,1,0) and (0,1,1) facets are energetically favourable for the surface oxide-alloy interface, while for the clean surface the regularly stepped (6,7,1) has the lowest surface free energy.

The structure of the long-range ordered oxide was determined to be the complex, ultrathin Al$_{10}$O$_{13}$ surface oxide that is known in detail from the oxidized NiAl(1,1,0) surface [7]–[10]. Our results show the step-induced preferential formation of one oxide twin-domain that is labelled ‘red’ in figure 5(d). Such favoured domain growth was also reported for NiAl(14,16,1) where strain release along the direction of the anti-phase domain boundaries (APDBs) is argued to be a possible reason [12]. Unlike their study, the APDBs, which run along the short axis of the oxide unit cells, are not aligned parallel to the step direction $\mathbf{a}_2$ for the NiAl(6,7,1) surface. Therefore this explanation does not hold for the preferential domain growth observed here. For the ordered surface oxide on NiAl(1,1,0) interfacial Al ions form pentagon–heptagon pairs as Al atoms prefer Ni neighbours [7]. These pairs are indicated as grey lines within the oxide unit cell in figure 5(d). They exhibit ‘dense’ quasi-rows of interfacial Al atoms running along certain directions. Along these rows, which are marked yellow in figure 5(d), increased strain is built up. Strain can be preferentially released along the steps ($\mathbf{a}_1$-direction). This favours the initial growth of the ‘red’ domain, where the Al quasi-rows are parallel to the $\mathbf{a}_1$-direction ([\(\overline{1}1\overline{1}\)]$_{\text{bulk}}$-direction), over the green domain. For the NiAl(14,16,1) it is reported that the step edges have a ragged shape with many sections running along the [\(\overline{1}1\overline{1}\)]$_{\text{bulk}}$-direction [12]. Therefore, this explanation would also hold for the preferential domain growth on NiAl(14,16,1).

5. Conclusions

The clean NiAl(6,7,1) surface consists of a regular sequence of identical, 14 Å wide (1,1,0) terraces and monoatomic (0,1,1) steps. A 0.23 and 0.12 Å buckling of Ni and Al atoms in the first and second rows is found, respectively. Al atoms relax outwards, Ni inwards. The atoms at the surface steps are relaxed towards the bulk, while atoms at the corner below the step relax outwards. These relaxations introduce strain fields around every surface step. The strain fields then interact with each other and lead to a step-step repulsion, which is crucial for the stability of the vicinal surface. Upon oxidation at 540 K and at $10^{-6}$ mbar of molecular oxygen for 900 s, a 5.5 Å thin, short-range ordered alumina film is formed on the surface while the regular pattern of terraces is maintained. The preferential Al oxidation produces a decrease of the Al concentration up to 13 Å within the alloy. Thereby the occurring Al-vacancies are accompanied by Ni anti-sites at a depth around 6 Å, whereas Ni vacancies are mainly found directly at the oxide–alloy interface. Strong relaxations in the first three rows towards the bulk are found probably due to the Al depletion. The strain fields around the steps are changed drastically, most likely lifting the

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step–step repulsion. During annealing of the oxidized sample in UHV the vitreous, short-range ordered oxide film transforms into the long-range ordered, ultrathin surface oxide, known from the oxidized NiAl(1,1,0) surface. At these high temperatures, the thermal energy is large enough to overcome the kinetic barriers for massive (1,1,0) faceting whereby widths over 50 times larger than those of the initial terraces are observed. By desorbing the oxide at temperatures above 1300 K, the initial (6,7,1) surface can be obtained again. Characterization of the surface oxide showed, that on the NiAl(6,7,1) surface mainly single domain oxide growth is observed, which is in contrast with a twin domain formation on NiAl(1,1,0). Strain, set up within Al rows at the oxide–alloy interface, can preferentially be released for the observed domain, where these Al rows run in the direction along the steps. During the initial formation of long-range ordered oxide this favours the growth of one twin domain over the other.

The results of the present study are of importance to the applications of alumina films on NiAl as nanotemplate or tunnelling barrier in future magnetic devices. The ideal support for metal clusters in catalytic model studies would be a highly reproducible, single domain, ultrathin, smooth, stable and homogeneous oxide film. Such properties are also needed for the further miniaturization of magnetic transistors. The work presented here shows that such ideal oxide films can be in principle realized by tailoring the oxide growth with surface steps running along dedicated directions. However, massive morphology changes of the interfacial region during the formation of the oxide film should be taken into account.

Acknowledgments

The authors are greatly indebted to R Henes, A Weible and A Weisshardt of the MPI for Metals Research for their help with sample growth and preparation. Furthermore we would like to thank the ID03 staff at the ESRF for help during the experiments.

References

[1] Schmid M, Kresse G, Buchsbaum A, Napetschnig E, Gritschneder S, Reichling M and Varga P 2007 Phys. Rev. Lett. 99 196104
[2] Franchy R 2000 Surf. Sci. Rep. 38 195
[3] Chen M S and Goodman D W 2008 J. Phys.: Condens. Matter 20 264013
[4] Desikusumastuti A, Qin Z, Staudt T, Happel M, Lykhach Y, Laurin M, Shaikhutdinov Sh and Libuda J 2008 Surf. Sci. 603 L9–13
[5] Luo M F, Huang J Y, Chiang C I, Hu G R, Wang C C, Wang C T and Lin C W 2009 Surf. Sci. 603 558–65
[6] Yi C-W and Szanyi J 2009 J. Phys. Chem. C 113 716–23
[7] Kresse G, Schmid M, Napetschnig N, Shishkin M, Koehler L and Varga P 2005 Science 308 1440
[8] Stierle A, Renner F, Streitel R, Dosch H, Drube W and Cowie B C 2004 Science 303 1652
[9] Jaeger R M, Kuhlenbeck H, Freund H-J, Wuttig M, Hoffmann W, Franchy R and Ibach H 1991 Surf. Sci. 259 235–52
[10] Libuda J, Winkelmann F, Bumer M, Freund H-J, Bertrams T, Neddermeyer H and Muller K 1994 Surf. Sci. 318 61–73
[11] Schmid M, Shishkin M, Kresse G, Napetschnig E, Varga P, Kulawik M, Nilius N, Rust H P and Freund H J 2006 Phys. Rev. Lett. 97 046101
[12] Ulrich S, Nilius N and Freund H-J 2007 Surf. Sci. 601 4603–7
[13] Franchy R, Eumann M and Schmitz G 2001 Surf. Sci. 470 337–46
[14] Somorjai G A and Van Hove M A 1989 Prog. Surf. Sci. 30 201–31

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[15] Westerstroem R et al 2007 Phys. Rev. B 76 155410
[16] Stierle A et al 2007 New J. Phys. 9 331
[17] Gustafson J et al 2006 Phys. Rev. B 74 035401
[18] Klikovits J et al 2008 Phys. Rev. Lett. 101 266104
[19] Prevot G, Steadman P and Ferrer S 2003 Phys. Rev. B 67 245409
[20] Walko D A and Robinson I K 1999 Phys. Rev. B 59 15446
[21] Vlieg E et al 2007 Surf. Sci. 601 4603–7
[22] Ferrer S and Comin F 1995 Rev. Sci. Instrum. 66 1674
[23] Robinson I K and Tweet D J 1992 Rep. Prog. Phys. 55 599–651
[24] Vlieg E 1997 J. Appl. Crystallogr. 30 532
[25] Vlieg E 2000 J. Appl. Crystallogr. 33 401
[26] Stierle A, Renner F, Streitel R and Dosch H 2001 Phys. Rev. B 65 165413
[27] Mullins D and Overbury S 1988 Surf. Sci. 199 141–53
[28] Steadman P, Peters K F, Isern H and Ferrer S 2001 Phys. Rev. B 64 125418
[29] Rahman T S, Kara A and Durukanoglu S 2003 J. Phys: Condens. Matter 15 S3197–226
[30] Le Goff E, Barbier L, Garreau Y and Sauvage M 2003 Surf. Sci. 522 143–60
[31] Al-Rawi A N, Kara A and Rahman T S 2004 J. Phys.: Condens. Matter 16 S2967–79
[32] Munkholm A and Brennan S 1998 J. Appl. Crystallogr. 32 5143–53
[33] Desjonqueres M C, Spanjaard D, Barreteau C and Raouafi F 2002 Phys. Rev. Lett. 88 056104
[34] Marchenko V I and Parshin A Y 1980 Sov. Phys.—JETP 52 129–31
[35] Smoluchowski R 1941 Phys. Rev. 60 661–74
[36] Stierle A 2009 private communication
[37] Meyer B and Faehnle M 1999 Phys. Rev. B 59 6072–82
[38] Vonk V, Ellinger C, Khoshidi N, Vlad A, Stierle A and Dosch H 2008 Phys. Rev. B 78 165426
[39] Bozzolo G, Amador C, Ferrante J and Noebe R D 1995 Scr. Metall. Mater. 33 1907–13