Segregation and reconstructions of Pt$_x$Ni$_{1-x}$(100)

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Abstract

It is known that on (100) surfaces of Pt$_x$Ni$_{1-x}$ single crystals Pt segregates. With increasing Pt concentration in the surface the transition from unreconstructed Ni(100) to the pseudo hexagonal Pt(100) reconstruction occurs via a shifted row reconstruction and several pseudo hexagonal (n × 1) superstructures (n = 7, 12 and 19) consisting of similar (7 × 1) and (5 × 1) subcells. This was revealed by atomically resolved scanning tunnelling microscopy (STM). From low energy ion scattering measurements it becomes clear that the formation of the pseudo hexagonal structure leads to strong amplification of Pt segregation. Chemically resolved STM on the atomic scale shows that Pt prefers the highly coordinated four-fold hollow sites in the pseudo hexagonal structures and Ni is pushed into nearly on-top or bridge sites. Therefore the strong tendency of Pt to increase its coordination is proposed as the driving force of the reconstructions. Corrugations and chemical ordering measured by STM within the pseudo hexagonal reconstructions are confirmed by simulations based on embedded atom method potentials. © 1997 Elsevier Science B.V.

Keywords: Alloys; Computer simulations; Low energy ion scattering; Scanning tunnelling microscopy; Single crystal surfaces; Surface segregation; Surface stress; Surface structure

1. Introduction

The (100) surfaces of the 5d fcc metals Au, Ir and Pt are found to be reconstructed with a pseudo hexagonal top layer [1]. Pt(100) exhibits a pseudo hexagonal reconstruction with a stable configuration ($N \frac{1}{2}$) ($N$ = 8–12) which is 0.7° rotated compared to the bulk lattice and an unrotated metastable configuration [2–5]. In contrast to the fcc 5d metals, the (100) surfaces of fcc 3d and 4d metals do not reconstruct. Alloying of Pt with the 3d metal Ni, therefore, allows to increase the reconstruction tendency gradually from unreconstructed Ni to Pt(100)hex. These alloys are not only interesting for the study of some problems concerning basic physics, but they are also used in industry as heterogeneous catalysts for the hydrogenation of unsaturated hydrocarbons [6]. Since the variation of the Pt concentration in the surface can improve the selectivity of hydrogenation of different molecules [7], it is of crucial importance to know the surface concentrations and structures for different preparations.

Preferential sputtering of Ni on Pt–Ni alloy surfaces forms a Pt enriched altered layer [8] of several atomic layers thickness. Thermodynamic segregation out of this altered layer during annealing can be used to cover a relatively wide range of surface concentrations for one bulk composi-
After annealing to 1000 K the altered layer was found to be dissolved in the bulk for Pt$_x$Ni$_{1-x}$(100) ($x=10$ and 25) [9,10] single crystals and the Pt surface concentration is approximately constant after any following annealing cycles. In thermodynamic equilibrium the first layer is enriched in Pt and the second layer is depleted in Pt with respect to the bulk concentration [11,12].

In Pt$_x$Ni$_{1-x}$(100) single crystals ($x=10$ and 25) a shifted row reconstruction was found by scanning tunnelling microscopy (STM) [9]. A combined low energy electron diffraction (LEED) and STM study on Pt$_{50}$Ni$_{50}$(100) showed pseudo hexagonal superstructures with mixed ($12 \times 1$) and ($19 \times 1$) unit cells [13], which were supposed to consist of ($5 \times 1$) and ($7 \times 1$) subcells. All these reconstructions have in common the fact that they can be lifted by adsorption of CO, NO or O$_2$ [2,9,14,15].

Although STM normally gives only topographic information this technique can also be used for the chemical analysis of surfaces. Especially for Pt alloys chemical resolution with STM was achieved for Pt$_{50}$Rh$_{50}$(100) [16] and depending on the STM tip for Pt$_{25}$Ni$_{75}$(111) [17]. Chemical resolution is also reported for dislocation induced ($2 \times 1$) structures on Pt$_{25}$Ni$_{75}$(110) [18].

It was the goal of this work to bridge the gap between the shifted row reconstruction [as seen on Pt$_{10}$Ni$_{90}$ and Pt$_{25}$Ni$_{75}$(100)] and the fully developed pseudo hexagonal reconstruction [seen on Pt$_{50}$Ni$_{50}$(100)] by studying the surface structure of a Pt$_{40}$Ni$_{60}$(100) single crystal.

## 2. Experimental

Sample preparation and measurements were performed in ultra-high vacuum (UHV) with a base pressure <10$^{-10}$ mbar. The scanning tunnelling microscope was a commercial Omicron micro-STM operated in constant current mode at negative sample bias. Surface composition was determined by low energy ion scattering (LEIS) at room and elevated temperatures in a different UHV chamber with equivalent preparation facilities. LEIS measurements were performed using 1 keV He$^+$ ions with a symmetric scattering geometry, a scattering angle of 120°, and the [001] direction lying in the scattering plane. Since the impact and exit directions are only 30° from the perpendicular, geometric effects such as shadowing play no role in scattering from the first monolayer. Quantification of the LEIS spectra was done using pure metal single crystal standards, the reproducibility of the surface concentration is estimated to be better than 2%.

To cover a wide range of surface compositions, we used different combinations of sputtering (Ar$^+$ 1–2 keV) and annealing (500–1100 K). By this we achieved Pt surface concentrations between 64 and 79% with a Pt$_{40}$Ni$_{60}$(100) single crystal. Whereas Ni is preferentially sputtered at room temperature, the high Pt concentration at elevated temperatures around 850 K (see Section 3.1 and Section 5) causes the preferential removal of Pt. Sputtering at such sample temperatures leads to the depletion of Pt in a thick subsurface region. Therefore, we could achieve the lowest Pt concentrations by sputtering at ca 850 K. The cleanliness of the sample was routinely checked by Auger electron spectroscopy (AES).

## 3. Experimental results

### 3.1. Surface composition

The topmost layer of Pt$_{10}$Ni$_{90}$ and Pt$_{25}$Ni$_{75}$(100) single crystals was found to be enriched in Pt by preferential sputtering [10]. By this process an altered layer is formed with a thickness of several atomic layers depending on the primary ion energy. After annealing to temperatures between 500 and 800 K segregation out of the altered layer additionally increased the amount of Pt in the surface of these crystals. Going further to higher temperatures the altered layer was dissolved into the bulk and the Pt surface concentration decreased from 29 to 12% and from 54 to 35% for Pt$_{10}$Ni$_{90}$ and Pt$_{25}$Ni$_{75}$(100), respectively (Fig. 1). These concentration ranges were also the only possible Pt surface concentrations which could be achieved on these crystals by different preparations (Fig. 2). The lowest values of the Pt concentration [12 and 35% Pt for Pt$_{10}$Ni$_{90}$ and...
Fig. 1. Surface composition of Pt$_x$Ni$_{100}$ (x = 10, 25 [9,10] and 40%) single crystals measured with LEIS after annealing to different temperatures. Measurements were taken at 450 K (or lower, depending on the annealing temperature). Arrows indicate the sequence of the temperatures.

Fig. 2. Range of the surface concentrations for Pt$_x$Ni$_{100}$ single crystals at room temperature reachable by different preparation techniques depending on the bulk composition (grey area). The dotted line indicates the Pt surface concentration after annealing to thermodynamic equilibrium and subsequent cooldown. Concentration regions for the different superstructures are given. Values for x > 40% are estimates only.

Pt$_{25}$Ni$_{75}$(100), respectively] were those after annealing to thermodynamic equilibrium.

For the Pt$_{40}$Ni$_{60}$(100) single crystal preferential sputtering leads to a concentration of 60% Pt in the first layer. LEIS measurements at room temperature reveal that segregation of Pt starts at higher temperatures (800 K instead of 500 K) than for crystals with less Pt in the bulk and the decrease of the Pt surface concentration after further increasing annealing temperatures (T > 1000 K) is much smaller (from 79 to 76% Pt) (Fig. 1). However, LEIS measurements at elevated temperatures show that the Pt enriched altered layer is dissolved in Pt$_{40}$Ni$_{60}$(100) between 800 and 1000 K and the Pt concentration in the surface decreases significantly in this temperature range (from 73 to 61% Pt). But during cooling of the sample, Pt segregates back to the surface (Fig. 3a) and gives a final Pt concentration of 76%. LEIS measurements during heating of the sample on a ramp function (dT/dt = 100 K min$^{-1}$) from room temperature up to 1050 K and cooling (dT/dt = -100 K min$^{-1}$ or slower for T < 600 K) down to room temperature (Fig. 3b) also show the dissolution of the altered layer during heating to temperatures > 950 K, and the gradual increase of the Pt concentration while cooling. Auger electron spectroscopy carried out during the same annealing procedure as for LEIS exhibits also the dissolution of the altered layer for T > 800 K. The AES Pt/Ni ratio is constant after annealing to 1050 K and during cooling down. Whereas LEIS is sensitive only to the first monolayer, AES averages over several layers. A constant Pt concentration as seen with AES and an increasing one for LEIS, leads to the conclusion that Pt segregates out of the second layer during cooling and the well known oscillating depth profile of the Pt concentration is formed [11].

The Pt surface concentration range which can be achieved on the Pt$_{40}$Ni$_{60}$(100) single crystal is from 60 to 79% Pt. The thermal equilibrium concentration of 76% is almost as high as the highest value of 79% Pt. This maximum concentration can only be found after annealing to 800–900 K where Pt segregates out of the altered layer and this altered layer is not dissolved into the bulk. Going from 25 to 40% Pt bulk concentration the Pt surface concentration after annealing to thermodynamic equilibrium changes within the possible range of producible surface concentrations from the lowest to the highest values (dotted line in Fig. 2).

3.2. Surface geometry

Whereas LEIS gives the chemical composition of the surface, STM can show the reconstructions depending on the amount of Pt. Up to a concentration of 13% Pt in the (100) alloy surface no reconstruction can be observed by STM. For Pt surface concentrations between 13 and 65% (Fig. 2) the surface exhibits a shifted row reconstruction [9]. It consists of single atom rows which are shifted in the direction of the row, that is, [011] or [01̅1] and they form locally a hexagonal structure (Fig. 4). Atoms within the shifted rows protrude 5–30 pm out of the surface. The range of Pt concentrations where shifted rows are observed, is extended from 13–53% Pt on Pt_{10}Ni_{90} and Pt_{25}Ni_{75} (100) [9] to 65% Pt on Pt_{40}Ni_{60}(100) in the present study. The number of shifted rows on the surface is increasing with Pt concentration, but the distance between two shifted rows is never closer than five next neighbour distances even in the case of 65% Pt in the surface, which is in agreement with Ref. [9].

Above 65% Pt in the surface (7 × 1) stripes in the [011] or [01̅1] direction are formed, coexisting with shifted rows. These stripes consist of eight atom rows with pseudo hexagonal arrangement lying on seven atom rows of the substrate (Fig. 4). In a (for example) [01̅1] oriented row [the “×1” direction of the (7 × 1) stripes] the atoms are not always in equivalent positions. Whereas atoms at the edge of a (7 × 1) stripe are always in hollow sites, atoms in the middle can be in on-top or bridge position. The atoms are slightly displaced in [011] direction, that is, perpendicular to the row direction. After one atom row reaches an on-top position the displacement direction is reversed and another row goes gradually to an atop position. These displacements lead to a sinusoidal modulation of the atom rows (Fig. 5) with a periodicity of roughly 50 atomic distances in the [011] direction, which is not very uniform, however. Along the row direction [01̅1] no displacement is observed by STM and the atomic distances are equal to the bulk value.

Further increase of the Pt surface concentration (>65%) leads to pseudo hexagonal reconstructions which coexist with (7 × 1) stripes. For surfaces which show (7 × 1) stripes or pseudo hexagonal structures atom rows in unreconstructed positions can also be observed. But these unreconstructed areas can never exceed a maximum width of five rows between the different reconstructed domains.

Above 70% Pt the whole surface exhibits pseudo hexagonal reconstructions (Fig. 6) and no more single (7 × 1) stripes are present. In contrast to the (N̅11) structure of pure Pt(100) [2], these hexagonal reconstructions are not rotated with
respect to the substrate and not contracted in one (the “×1” or [011]) direction, as can be seen in regions were unreconstructed substrate lattice and pseudo hexagonal reconstructions coexist (Fig. 4) and at step edges. Atoms within the deepest lying rows of the pseudo hexagonal reconstruction (in Figs. 4 and 6) also have constant height, which indicates that they have the same position relative to the bulk, and therefore the reconstructed layer is not rotated or compressed along [011].

The pseudo hexagonal superstructures can be described as consisting of (19 × 1) and (12 × 1) cells [13]. Both types of cells can be thought to consist of (7 × 1) and (5 × 1) subcells (19 = 7 + 7 + 5; 12 = 7 + 5). Such a splitting in subcells is useful because after these distances (5 or 7) one atom row is in an unreconstructed position. LEED showed that there must be a larger periodicity in the arrangement of the subcells which leads to a (19 × 1) or (12 × 1) structure [13]. Whereas (5 × 1) subcells are symmetric with no oscillations of the atom positions, (7 × 1) subcells exhibit a similar wobbling of the on-top rows as described for the (7 × 1) stripes above. Only in one of the two (7 × 1) subcells of a (19 × 1) unit cell one atom is in atop position, in the other (7 × 1) subcell the three atoms in the middle are near a bridge site (Fig. 6). Therefore the (19 × 1) structure can also be seen as a reconstruction of its own, consisting of one (5 × 1) and two (7 × 1) building blocks. The (7 × 1) stripes are shifted parallel to each other in that way, that only one (7 × 1) subcell exhibits a on-top row within one (19 × 1) unit cell.

LEED studies on Pt₅₀Ni₅₀(100) [13] showed a varying distribution of the structure types with varying preparation. Increasing Pt concentration increased the amount of (5 × 1) sub cells which have a higher density of atoms than (7 × 1) subcells (Table 1). We were not able to make such statistics out of our STM images of fully pseudo hexagonal reconstructed surfaces on the Pt₄₀Ni₆₀(100) crystal, because we had only a small concentration region (70–79% Pt) where the whole surface is pseudo hexagonal reconstructed. However, if we increase the Pt concentration from 65% Pt, where only shifted rows are observed, to a Pt surface concentration with a beginning formation of pseudo hexagonal structures, we never found shifted rows close to (19 × 1) structures. The only pseudo hexagonal structure observed coexisting with shifted rows, is a (7 × 1) structure. With further increasing Pt concentration (7 × 1) structures were found to be near to a (19 × 1), but not to a (12 × 1) structure. In other words, with increasing amount of Pt in the surface the (7 × 1) structures are observed earlier than the (5 × 1) subcells. This leads to the
Fig. 5. $3 \times 10$ nm$^2$ constant current topograph ($U_{tip} = -0.5$ mV, $I_t = 0.9$ nA) of a (7 × 1)hex stripe with wobbling of the on-top rows. The shift of the atomic positions is indicated by the lines which mark the positions for the case row No. 5 is in atop position (in the middle of the STM image). The model shows how the on-top position switches from row 5 to 3. The colour of the atoms in the model indicates the apparent height of the atoms.

Conclusion that a (5 × 1) subcell consists of more Pt than a (7 × 1), which confirms the LEED observation on Pt$_{50}$Ni$_{50}$(100) [13].

The measured corrugation on Pt$_{40}$Ni$_{60}$(100) perpendicular to the rows (100 pm, Fig. 6) is similar to the corrugation of Pt(100)hex reported in the literature (Refs [2] and [19], 100 pm and 50–72 pm, respectively). The rows adjacent to on-top rows are not resolved by STM because of the big differences in height, only in regions where the rows are of similar height are all atoms visible (Fig. 6).

The mean next-neighbour distance (relative to the bulk next-neighbour distance) between atoms in adjacent rows in pseudo hexagonal structures is decreasing with an increasing Pt surface concentration (Table 1). Whereas in the (7 × 1) reconstructions this distance is larger than the bulk next-neighbour distance, it is smaller for all other quasi hexagonal structures. The distance in the "×1" direction remains the bulk value.

The length of quasi hexagonal stripes of (7 × 1), (12 × 1) and (19 × 1) is only limited by step edges or impurities (Fig. 7) and reaches >100 nm. Similar to an unrotated quasi hexagonal layer on Pt(100) [2] the stripes are parallel to step edges. The shortest observed stripes are at least 10 nm long.

Carbon is known as the main impurity on Pt$_x$Ni$_{1-x}$ surfaces and for reducing the density of...
Fig. 6. A 10 x 8 nm² constant current topograph of a pseudo hexagonal superstructure \((U_{bg} = -0.5 \text{ mV}, I_t = 12.9 \text{ nA})\) on Pt_{40}Ni_{60}(100) with 72% Pt in the first monolayer. The atomic corrugation along the [01\] direction is 20–30 pm. Buckling of the first monolayer is up to 100 pm. A linescan calculated out of our EAM simulations of the (19 x 1) structure is given for comparison with linescan B-B'.

Table 1

<table>
<thead>
<tr>
<th>Reconstruction</th>
<th>(7 x 1)</th>
<th>(19 x 1)</th>
<th>(12 x 1)</th>
<th>(5 x 1)</th>
<th>(\frac{N}{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface/bulk atoms per unit cell</td>
<td>8.7</td>
<td>22/19</td>
<td>14/12</td>
<td>6/5</td>
<td>76/61</td>
</tr>
<tr>
<td>Reconstruction atom density/density of unreconstructed layer</td>
<td>1.14</td>
<td>1.16</td>
<td>1.17</td>
<td>1.2</td>
<td>1.25</td>
</tr>
<tr>
<td>(d_{surface}/d_{bulk})</td>
<td>1.008</td>
<td>0.997</td>
<td>0.992</td>
<td>0.972</td>
<td>0.966</td>
</tr>
</tbody>
</table>

\(d_{surface}\) is the average inter-atomic distance in the surface layer between atoms in adjacent rows (assuming a flat surface layer). The inter-atomic distance within a row in a non-rotated pseudo hexagonal reconstruction is the bulk value. Atom density for the \(\frac{N}{1/2}\) reconstruction from Ref. [5].

states around the Fermi energy. Carbon is therefore only visible as “dark” region on the surface [20] (Fig. 4). STM (Fig. 6) and the absence of carbon in Auger spectra of the fully reconstructed surfaces show that carbon is not, however, found in the reconstructed areas of the surface. So the pseudo hexagonal reconstructions are not induced by any impurity.

3.3. Chemical structure on the atomic scale

Chemically resolved images (Fig. 8) have been obtained on the pseudo hexagonal reconstructions under special tip conditions similar to Pt_{35}Ni_{25}(111) [17]. Sometimes the formation of a tip with chemical resolution occurred while scanning but was not reproducible under controlled
conditions. As proposed in Refs [17] and [21] an adsorbate on the tip may change the interaction between the tip and sample wave functions by either a kind of precursor of chemical binding between the adsorbate and a substrate atom, or by reducing the tip–sample distance and leading to a stronger interaction between the tip and sample.

Identifying the “bright” species in Fig. 8 as Ni, we found good agreement between chemical analysis by atom counting (76% Pt in Fig. 8) and LEIS (78% Pt) carried out after identical sample preparation. The counting of atomic species cannot be done by a histogram of the apparent height as in Refs [17] and [16], because the chemical contrast of 20–60 pm is superimposed by the corrugation of the pseudo hexagonal reconstruction perpendicular to the rows of ca 100 pm. It is interesting to note that the chemical contrast is larger in low coordinated rows (linescan A, Fig. 8) than in rows with higher coordination and therefore deeper positions (linescan B, Fig. 8). For counting the atoms, each atom has to be compared with its neighbours in the [011] direction and than it can be decided whether it is a “dark” or a “bright” atom. All atoms which are hidden by bright adja-
Fig. 8. Atomically and chemically resolved constant current topograph of Pt$_{40}$Ni$_{60}$(100) with the same reconstruction as in Fig. 6 (10 × 9 nm$^2$, $U_{tip} = -0.5$ mV, $I_t = 4$ nA). This image shows 24% bright and 76% dark atoms. Bright atoms are identified as Ni by comparison with LEIS (22% Ni and 78% Pt). The arrows indicate the linescan positions. The chemical contrast between Ni and Pt atoms is 20–60 pm. The numbers indicate the Pt concentrations (%) in the marked rows.

cent atoms (10%) are counted as “dark”. Fig. 8 shows that Ni is mainly found in positions which are geometrically higher, i.e., low coordinated sites, whereas the lower rows, i.e., higher coordinated sites consist entirely of Pt. The good agreement between LEIS and STM also demonstrates the high accuracy of surface concentrations determined by LEIS.

4. Simulations

We performed MC (Monte Carlo) and MD (molecular dynamics) simulations to study the corrugation and chemical arrangement of the pseudo hexagonal reconstructions. We used the embedded atom method (EAM) [22] based on potentials of Ref. [23], which were optimized for the PtNi system [18]. The simulated cells consisted of a 13 layer slab with seven atoms in the [011] direction and 7, 12 or 19 atoms in the [011] direction in the bulk and 8, 14 or 22 atoms in the first layer for the different pseudo hexagonal structures. Atoms in the top-most layer were initially placed in a flat hexagonal arrangement. The simulation runs were performed as iterative sequence of MD and MC. First the simulation configuration has been allowed to relax to equilibrium in the MD run. Afterwards we performed MC simulation to calculate the correct chemical distribution. Subsurface atoms and partly also the first layer atoms were free to move. Then we restarted with MD and so on. The bulk chemical composition was adjusted by choosing of the right difference of the chemical potentials ($\Delta \mu$) for Pt and Ni.

The pseudo hexagonal reconstructions were not stable with the current potentials. To stabilize the reconstruction, we restricted the movement of first layer atoms perpendicular to the surface and in the [011] direction during the MD runs. During
the MC simulations we fixed the positions of the atoms adjacent to the on-top rows. All other atoms were free to move in any direction. Without these constraints the top layer changed to an added row reconstruction during the simulation runs. When the atoms had reached their equilibrium site and composition we were able to skip the constraints in movement and the $(7 \times 1)$ and $(12 \times 1)$ reconstructions stayed stable for $2-3 \times 10^6$ MC steps. However the $(19 \times 1)$ reconstruction changed immediately to an added row reconstruction. Fig. 9 gives the average positions and compositions for the topmost part of the simulation cell for the $(12 \times 1)$ reconstruction during the $2 \times 10^6$ MC steps. The 12-layer bulk below the top layer consists of 47% Pt and the top layer consists of 70% Pt. This value is slightly smaller than that found by LEIS measurements on Pt$_{40}$Ni$_{60}(100)$ with 76% Pt in the first layer.

The most important information can be obtained if the concentration for different sites is analysed. Four-fold hollow positions (10 next neighbours) are occupied almost exclusively by Pt. Ni atoms are placed mainly in the on-top sites (Ni concentration > 73%) and below the highly coordinated Pt atoms (Ni > 90%) (Fig. 9). Chemically resolved STM images show a larger difference of the Pt concentration between the on-top rows and adjacent to on-top rows (Table 2 and Fig. 8), which can also be attributed to the trend of the simulation to underestimate segregation. The comparison of a linescan of an STM image with the simulated $(19 \times 1)$ top layer (without the constraints removed) shows the very good agreement between the corrugation of STM and simulation (Fig. 6 linescan B–B'). This agreement justifies the constraints applied during the simulation. Only the on-top positions seem to be too high in the simulation, but this can be attributed to the tendency of the simulation to form added rows. Furthermore the linescan of the simulated structures gives the positions of atomic cores, whereas STM can show lines of constant density of states in a distances of ca 3–4 Å above the surface, which can, however, be different.

5. Discussion

The Pt concentration on the surface of a Pt$_{40}$Ni$_{60}(100)$ single crystal increases during cooling from 1000 K to room temperature (Fig. 3b), and the surface exhibits a pseudo hexagonal reconstruction after this treatment. Pt$_{15}$Ni$_{85}(100)$ and Pt$_{25}$Ni$_{75}(100)$ have neither a pseudo hexagonal reconstruction [9] nor does the Pt surface concentration increase during cooling (Fig. 1). So the strong segregation of Pt on Pt$_{40}$Ni$_{60}(100)$ seems to be coupled to the existence or formation of pseudo hexagonal reconstructions during cooling of the crystal. Although we had no possibility to observe the structure of the surface at elevated temperatures, it is likely that the surface of Pt$_{40}$Ni$_{60}(100)$ is not hexagonal reconstructed at 1000 K because at this temperature the surface consists of 62% Pt (Fig. 3b) and this value is too low to form a pseudo hexagonal reconstruction, which needs a least 70% Pt (if measured at room temperature).

Chemically resolved STM images of the reconstructed surface reveal that Ni is pushed into low coordinated sites whereas Pt occupies higher coordinated sites. This agrees nicely with the segregation behaviour of Pt$_x$Ni$_{1-x}$ alloys in general, where closed packed surfaces like (111) and (100) are enriched in Pt by segregation [12,10] and the
Table 2
Comparison between the average Pt concentration of STM and EAM simulation in different sites of the reconstruction

<table>
<thead>
<tr>
<th>Reconstruction site</th>
<th>On-top</th>
<th>Adjacent on-top</th>
<th>Four-fold hollow</th>
<th>Adjacent four-fold hollow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt concentration (%)</td>
<td>STM (Fig. 8) 10</td>
<td>98</td>
<td>97</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Simulation (Fig. 9) 21</td>
<td>68</td>
<td>99</td>
<td>68</td>
</tr>
</tbody>
</table>

open (110) surface (with a smaller number of next neighbours at the surface) is enriched in Ni [10, 11]. These chemical distributions as well as the corrugations of hexagonal reconstructions are confirmed by our MD and MC simulations with EAM potentials.

In the literature [24, 25] it is proposed that the pseudo hexagonal reconstructions of the (100) surfaces of the 5d metals Au, Ir and Pt are driven by the reduction of tensile stress and the reconstruction should decrease next neighbour distances within the surface and increase the density of surface atoms. Whereas this density is increased by ca 25% on Pt(100)hex and by 16% for (19 x 1), the reduction of next neighbour distances is 4% for pure Pt, but negligible for (19 x 1). The mean inter-atomic distance in the first layer of a hex(7 x 1) cell is even slightly larger than the bulk value (see Table 1). Therefore the existence of the (19 x 1) and (7 x 1) structures cannot be driven by the relief of tensile stress, that is, the tendency to reduce the bond length at the surface. This is already neutralized by Pt segregation moving the larger Pt atoms to the first monolayer.

The mean value of the coordination number of the first and second monolayer atoms is decreased by quasi hexagonal reconstructions as mentioned in Ref. [24], but only for the first monolayer it is increased. The energy difference for changing the coordination number is larger for atoms with low coordination than for atoms with higher coordination [26] (this is shown in Table 3). The energy gain of additional bonds in the surface can therefore exceed the energy loss for the lost coordination in the second monolayer. From this one has to conclude that the trend of Pt to increase its coordination number is the main reason for the reconstructions on PtₓNi₁₋ₓ(100) and Pt(100) surfaces.

Another argument against the relief of tensile stress as the main reason for the quasi hexagonal reconstruction is the existence of (7 x 1) and shifted rows close together (Fig. 4). Shifted rows neither increase the density of atoms on the surface nor do they decrease the next neighbour distance [9] (in fact an increase of 11% is observed). But whereas the coordination number of atoms within the shifted rows stays the same, for the adjacent rows it is increased from eight to nine. Again, the price to pay for this reconstruction is a reduced coordination in the second layer, from 12 to 10 for the atoms below the shifted rows.

In contrast to Ni, Pt has a significantly lower surface energy at the (111) face compared to the unreconstructed (100) surface (Table 3), even when referred to the area (J m⁻²), in spite of the larger number of atoms at these surfaces. Therefore Pt has an especially strong tendency to form hexagonal surfaces.

6. Summary

LEIS measurements on a Pt₄₀Ni₆₀(100) single crystal revealed a strong segregation of Pt during cooling from 1000 K to room temperature. Since this behaviour was not observed on crystals with less Pt bulk concentration, where no pseudo hexagonal reconstructions were observed, it may point to a segregation promoted by the formation of the pseudo hexagonal reconstruction.

Atomically resolved STM images of Pt₄₀Ni₆₀ (100) surfaces with shifted row and pseudo hexagonal super-structures depending on the Pt concentration have been presented. The (12 x 1) and (19 x 1) structure were found to consist of (7 x 1) and (5 x 1) subcells. Whereas the (5 x 1) is central symmetric, atoms within a (7 x 1) slightly change their positions perpendicular to the “x 1” direction from one unit cell to the next. In chemically resolved STM images of pseudo hexagonal super-
structures Ni atoms are found to be located in low coordinated sites of the reconstruction, whereas Pt atoms tend to stay in high coordinated sites. This and the corrugation of the reconstructions is also confirmed by the EAM simulations.

Given the fact that neither the shifted row reconstruction nor the pseudohex reconstruction of Pt$_{x}$Ni$_{1-x}$(100) lead to a significant reduction of bond lengths, tensile stress relief is not believed to be the main reason for promoting the reconstructions. We propose that the reconstructions are rather caused by the tendency of low-coordinated surface atoms to increase their coordination number and by a strong tendency towards a hexagonal first layer.

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References