Temperature-dependent segregation and (1 × 2) missing-row reconstruction of Pt$_{25}$Rh$_{75}$(110)

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Abstract

The surface structure and composition of the clean Pt$_{25}$Rh$_{75}$(110) surface is investigated by low energy electron diffraction (LEED) and low energy ion scattering (LEIS). For the equilibrated Pt$_{25}$Rh$_{75}$(110) surface we observe a (1 × 2) missing-row reconstruction in analogy to the pure Pt(110) surface, and a significant Pt enrichment of the topmost atomic layer (up to 80 at. % Pt). As the same strong surface enrichment in Pt was found in a previous study on the (100) and (111) surface of the same bulk composition, this means that in contrast to Pt–Ni and Pt–Co alloys, for Pt$_{25}$Rh$_{75}$ alloys the segregation behavior is not influenced extensively by the surface orientation. In addition to the structure analysis by LEED we performed LEIS experiments to determine the temperature-induced changes of the surface composition and structure. Since the Pt segregation is less pronounced at elevated temperature, the surface reveals a temperature-induced deconstruction of the (1 × 2) structure around 750 °C, resulting in an fcc(110) (1 × 1) surface at high temperature. Temperature-dependent measurements further show a hysteresis-like behavior of the top-layer composition, which is attributed to an enhanced Pt segregation on the (1 × 2) reconstructed surface. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Pt–Rh alloys are applied in the so-called three-way catalyst for automotive pollution control, and also play an important role for the industrial production of nitric acid and hydrogen cyanide. Besides their excellent catalytic properties (e.g. oxidation of CO and simultaneous reduction of NO [1]) PtRh alloys are appreciated because of their high resistance to corrosion and their outstanding thermal stability.

The wide field of technical application has motivated intensive investigations of the surface segregation in Pt–Rh, indicating an extraordinary behavior of Pt–Rh in the group of Pt-based binary alloys: since Pt and Rh are rather similar, with a size difference of only 3% (Rh is smaller) and quite small excess quantities for the mixture, surface segregation is mainly driven by the difference in the surface enthalpy values of the components (Pt segregation). Owing to the low excess value of Pt–Rh mixing enthalpy there is no long-range ordered phase in the whole range of composition [2]. Hence, ordering tendencies in the near-surface region have no important influence on the segregation behavior. This is in contrast to other Pt alloys such as Pt–Ni [3–5] or Pt–Co [6–8], where...
a strong tendency towards an alternating layer composition is found, which results in a reversed Pt segregation on the (110) surfaces despite the tendency of Pt to segregate [9,10]. Regarding such considerable orientational effects on the segregation behavior, the present study may contribute to the general understanding of surface segregation, giving detailed data on the layer-resolved composition and surface structure of Pt_{25}Rh_{75}(110). Based on two independent experimental methods, low energy electron diffraction (LEED) and low energy ion scattering (LEIS), the orientational dependence of surface segregation is characterized and compared with recent results for the Pt_{25}Rh_{75}(100) and (111) surface [11] obtained with the same experimental setup.

In accordance with the systematic trends of Pt-metal alloys [8], most experimental data for the Pt-Rh (100) and (111) surfaces describe a strong Pt segregation over the whole temperature range and for all bulk compositions studied (in the absence of contamination, e.g. see Refs. [11–16]). This behavior was also confirmed theoretically by tight-binding Ising model calculations [17], thermodynamic multilayer model calculations [18] and recent first principles calculations [19]. Concerning the Pt_{25}Rh_{75}(110) surface investigated in this study, theoretical calculations [18,20] predict a similar trend towards Pt segregation as found experimentally on the Pt_{25}Rh_{75}(100) and (111) surfaces [11], where the Pt concentration in the top layer reaches up to 80 at.% on the equilibrated surface. However, a considerable Pt enrichment of the Pt_{25}Rh_{75}(110) surface might involve a surface reconstruction similar as the Pt_{80}Fe_{20}(110) (1×2) [21] or the pure Pt(110) (1×2) surface [22]. Such a (1×2) missing-row reconstruction was observed on Pt_{25}Rh_{75}(110) after equilibrating at high temperature and will be analyzed in Section 3.1. Nevertheless, as surface segregation is generally less enhanced at elevated temperature, the temperature-related reduction of the Pt enrichment leads to a deconstruction at high temperature. To separate clearly the structure analysis from temperature-dependent measurements, we subdivide Section 3 into two parts. The first part describes a full LEED I–V structure analysis of the equilibrated Pt_{25}Rh_{75}(110) surface, revealing a (1×2) missing-row reconstruction. In the second part LEIS measurements are presented which describe the temperature-dependent surface composition, and owing to the structural knowledge and a favorable scattering geometry, a temperature-induced structural change of the surface structure.

2. Experimental

All measurements were performed in the same ultra high vacuum chamber at a residual gas pressure below 1×10^{-10} mbar. The Pt_{25}Rh_{75}(110) surface was prepared by cycles of sputtering and annealing (T=900 °C) until a sharp LEED pattern with very low background was reached. The cleanness of the sample was checked by Auger electron spectroscopy (AES) before and after measurement, indicating the absence of impurities such as S or C within the sensitivity limit of AES.

LEED measurements were done at room temperature at normal incidence (crystal misalignment less than 0.1°) using a commercial two-grid back view optics and video data acquisition. The Earth’s magnetic field was shielded by more than 90% through a mu-metal chamber. All the LEED image data were recorded as eight-bit images in energy steps of 1 eV and analyzed subsequently by image processing. The intensity versus energy (I–E) curves were normalized to the emission current of the electron gun, averaged over equivalent beams, background subtracted and smoothed in the Fourier domain.

LEIS measurements were done at variable temperature with a primary He^+ ion beam of 1 keV energy (current density 10 nA mm^{-2}). The energy of the scattered ions was analyzed at constant resolution with a hemispherical electrostatic energy analyzer. The energy spectra were recorded for two scattering angles (θ=60° and θ=120°) between room temperature and 1100 °C. The quantification of the top-layer composition was done as described in a previous study [11] by means of a least-squares fit of standard spectra to the alloy spectra, taking into account the differing atomic densities of the pure metals. The standard spectra
were obtained by LEIS measurements on the annealed Pt(111) and Rh(111) surfaces at room temperature under identical scattering conditions. We checked carefully that sputter-induced surface damage did not alter the measured surface composition during the time of one measurement (about 20 s). Furthermore, we confirmed the temperature independence of the standard spectra as known from a similar LEIS study [23].

3. Results and discussion

3.1. Structure analysis

After annealing the sputtered Pt$_{25}$Rh$_{75}$(110) surface at 950 °C for 5 min and subsequently cooling to room temperature, a sharp and reproducible (1 × 2) superstructure with 2 mm symmetry is exhibited. In analogy to the well known missing-row reconstruction of Pt(110) [22], Au(110) [24] or PtnFe$_{2}$(110) [21], we started our LEED intensity calculations using the missing-row structure model sketched in Fig. 1. Among 16 fit parameters we adjusted the interlayer distances and chemical concentrations of the topmost four atomic layers, including symmetry consistent distortions as a lateral shift (pairing $\Delta y_{2}$) in the second atomic layer and a vertical shift (buckling $\Delta z_{3}$) in the third atomic layer. The non-structural parameters were two spherically isotropic vibration amplitudes for atomic sites in the top layer and the second layer (no distinction between Pt and Rh made), and the real and imaginary part of an energy-independent inner potential. The calculation of the $I$–$V$ curves was carried out by use of the Van Hove subroutines [25] and tensor-LEED [26]. The atomic phase shifts were calculated relativistically by self-consistent Dirac–Slater wave functions [27]. The layer-dependent composition of the substitutionally disordered Pt$_{x}$Rh$_{1-x}$(110) layers was described by the average $\sigma$-matrix approximation [28,29]. The search for the best-fit structure was facilitated by a stochastic search algorithm based on simulated annealing [30], where all structure parameters and the vibration amplitudes could be varied simultaneously. For the optimized structure parameters we used an experimental data set of 16 non-equivalent reflections (9 integral and 7 fractional) giving rise to a total energy overlap of 4900 eV. The degree of agreement was evaluated by the Pendry reliability factor [31].

The missing-row model (Fig. 1) achieves a satisfactory agreement between calculation and experiment, that is expressed by a Pendry reliability factor $R_{p} = 0.24$. The convincing agreement of the calculated and experimental intensity curves is shown in Fig. 2. The corresponding geometrical and structural parameters are given in Table 1. Concerning the chemical composition of the near-surface region, we notice a significant Pt enrichment of atomic sites in the (111) micro facets up to 80 at. % Pt in the top layer (denoted by $C_1$, $C_2$, and $C_3$ in Fig. 1), and a Pt depletion of the third layer atomic site which is buried by the top layer (denoted by $C_3$ in Fig. 1). This behavior agrees well with former results obtained for the PtnRh$_{2}$(111) surface, where the topmost layer was Pt enriched, and the second layer, which corresponds here to the atomic site $C_3$ with respect to the (111) micro facet, was Pt depleted (e.g. [11]). The chemical composition of the fourth
Fig. 2. Experimental and calculated $I$--$V$ curves of the 16 beams used for the intensity analysis of the equilibrated Pt$_x$Rh$_{1-x}$(110) surface. The dotted lines are the calculated intensities, the solid lines are the experimental intensities. The calculated lines have been shifted upwards for better visibility. The associated Pendry reliability factor is $R_p=0.24$. 
Table 1: Best fit parameters of the equilibrated clean Pt$_{25}$Rh$_{75}$ (110) surface.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Best-fit value</th>
<th>Error bars</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_1$</td>
<td>80</td>
<td>17</td>
<td>at. %</td>
</tr>
<tr>
<td>C$_2$</td>
<td>45</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>C$_3$</td>
<td>10</td>
<td>24</td>
<td></td>
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<tr>
<td>C$_4$</td>
<td>40</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>C$_5$</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_6$</td>
<td>25</td>
<td></td>
<td>fixed</td>
</tr>
<tr>
<td>$d_{12}$</td>
<td>$-0.10$</td>
<td>$-0.29$</td>
<td>Å</td>
</tr>
<tr>
<td>$d_{23}$</td>
<td>$-0.08$</td>
<td>$-0.10$</td>
<td>Å</td>
</tr>
<tr>
<td>$d_{34}$</td>
<td>$-0.02$</td>
<td>$-0.01$</td>
<td>Å</td>
</tr>
<tr>
<td>$d_{45}$</td>
<td>$0.00$</td>
<td>$0.00$</td>
<td>Å</td>
</tr>
<tr>
<td>$d_{5b}$</td>
<td>1.35 (1.39)</td>
<td></td>
<td>Å</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>$0.02$ (0.04)</td>
<td></td>
<td>Å</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>$0.13$ (0.17)</td>
<td></td>
<td>Å</td>
</tr>
</tbody>
</table>

The contraction of the interlayer spacings of the near surface layers is similar but less pronounced than on the clean Pt(110) (1×2) surface [22] (see Table 1). We observe a significant distortion of the three topmost layers caused by contractions of the layer distances $d_{12}$ and $d_{23}$ and a buckling ($\alpha_z = 0.13$ Å) in the third atomic layer. The layer distances and concentrations underneath are almost equal as in the Pt$_{25}$Rh$_{75}$ bulk. Since the lateral shift $y_2$ in the second layer was very small, and near the limit of sensitivity, a lateral distortion of the forth layer was not considered in the calculation.

The error bars in Table 1 are based on the variance defined by Pendry [31] and were calculated by total parameter variations (i.e. when varying one parameter all other parameters were re-adjusted), so that coupling between parameters (including the vibration amplitudes) was included in the determination of the error bars. The estimated error bars for the chemical composition are in the range of 50%, and seem rather pessimistic with respect to the reasonable results obtained by LEED $I$-$V$ analysis on other Pt-Rh surfaces despite comparably large error bars [11], or considering a recent case study for Pt-Rh indicating considerably smaller error bars for the chemical parameters than those derived from the Pendry variance [32]. A further indication of much better accuracy than that indicated by the error bars is the comparison of our results for the top-layer composition of Pt$_{25}$Rh$_{75}$ (110), derived on the same crystal by three independent experimental techniques, LEED (80 at.% Pt, see Fig. 3), LEIS (82 at.% Pt, Ref. [33]) and scanning tuneling microscopy (STM) (81 at.% Pt, see Section 4) and scanning tuneling microscopy (STM) (81 at.% Pt, Ref. [33]).

Although our best-fit reliability factor of $R_p = 0.24$ is lower than the Pendry $R$-factors

The three topmost layers is C=44%, i.e. the near surface region is considerably enriched with Pt. For comparison, on the Pt$_{25}$Rh$_{75}$ (100) surface there was almost no change of the average composition (in four layers) after equilibration and on the Pt$_{25}$Rh$_{75}$ (11) surface there was only a comparably small increase of the average composition (C=36 at.% Pt) [11].

The high Pt concentration in the near-surface region might be essential for the Pt(110)-like missing-row reconstruction.

atomic layer is practically not changed with respect to the bulk composition. The calculated chemical composition of Pt$_{25}$Rh$_{75}$ (110) is shown in Fig. 3 as depth profile. The average Pt concentration of the Pt$_{25}$Rh$_{75}$ (110) surface after annealing at 950°C and subsequent cooling. We find a significant Pt enrichment of 80 at.% in the topmost layer, but also Pt enrichment of second- and third-layer atomic sites in the (111) facets. The 'buried' atomic site in the third layer, which corresponds to a second layer with respect to the (111) facet (see Fig. 1), is Pt depleted (10 at.% Pt). The average composition in the three topmost surface layers C=44 at.% Pt indicates the considerable Pt enrichment of the surface.

Fig. 3. Layer concentrations of the Pt$_{25}$Rh$_{75}$ (110) surface after annealing at 950°C and subsequent cooling. We find a significant Pt enrichment of 80 at.% in the topmost layer, but also Pt enrichment of second- and third-layer atomic sites in the (111) facets. The 'buried' atomic site in the third layer, which corresponds to a second layer with respect to the (111) facet (see Fig. 1), is Pt depleted (10 at.% Pt). The average composition in the three topmost surface layers C=44 at.% Pt indicates the considerable Pt enrichment of the surface.

Although our best-fit reliability factor of $R_p = 0.24$ is lower than the Pendry $R$-factors
achieved by former LEED studies of missing-row reconstructions (e.g. $R_p = 0.36$ for Pt(110) [22] and $R_p = 0.35$ for Au(110) [24]), the excellent agreement found in our previous LEED studies [12] [11] is not reached. The comparably higher reliability factor of this intensity analysis might result from non-isotropic vibration amplitudes in the reconstructed top layer, or the space-dependent inner potential due to the atomic roughness of the missing-row structure, as both are neglected in the LEED calculation using the standard codes. Moreover, the remaining misfit between calculation and experiment is generally increased by limited domain sizes of the surface reconstruction and a high step density on the surface, both observed by STM on the same surface [33].

In spite of the fact that the existence of alternative structures (sawtooth model, hollow on facet, ridge model [34]) seems very unrealistic with regard to the well-known tendency of Pt towards missing-row reconstruction, the definite confirmation of the missing-row structure was achieved by analyzing STM image data of the same Pt$_{25}$Rh$_{75}(110)$ surface (to be published by co-authors in Ref. [33]). The STM scans clearly indicate the existence of close-packed atomic rows along the [110] direction of the (110) surface, with a separation corresponding to the top-layer rows of the (1$x$2) missing reconstruction. Owing to chemical contrast between Pt and Rh, the top-layer composition of the equilibrated Pt$_{25}$Rh$_{75}(110)$ surface could be determined by STM to 81$\pm$2 at.$\%$ Pt [33]. This value is in excellent agreement with the top-layer composition determined by LEED intensity analysis ($C_{1} = 80$\pm 2 at.$\%$ Pt).

In contrast to the missing-row reconstructed Pt$_{80}$Fe$_{20}$(110) (1$x$2) surface [21], where chemical ordering in the dense rows along the [110] direction was found (giving rise to weak extra spots in the LEED pattern), on Pt$_{25}$Rh$_{75}$(110) we did not find any evidence for chemical ordering in the electron diffraction pattern. This agrees well with the very low tendency towards chemical ordering in bulk [2] and the topmost layers of the low index surfaces of Pt$_{25}$Rh$_{75}$ [33]. This is why no further LEED $I-V$ calculations were done to exclude alternative missing-row models with an ordered second or third atomic layer.

### 3.2. Temperature-dependent surface segregation

The temperature-dependent top-layer composition of Pt$_{25}$Rh$_{75}$(110) was determined by LEIS using a scattering geometry where the trajectories of the incoming and outgoing ions are along the crystallographic [011] and [011] directions, respectively (see Fig. 4). These particular scattering conditions imply a geometrical shadowing (and blocking) of all atoms in atomic layers underneath the topmost layer. Regarding the generally low survival probability of 1 keV He$^+$ ions and especially the low cross-section for double scattering, possible only in the plane of the top layer, the measured ion signal results solely from single elastic scattering by atoms of the topmost layer. This fact is also reflected by the LEIS spectra, where neither a broadening of the single elastic scattering peaks of Rh and Pt (with respect to the standard spectra) nor an additional scattering intensity was detected. The quantification of the top-layer com-

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**Fig. 4.** Scattering geometry where deeper atomic layers (dark atoms) of the fcc(110) surface are geometrically shadowed and blocked by the topmost layer. Possible scattering trajectories and shadow/blocking cones are indicated (scattering angle $\theta = 60^\circ$, incidence angle $\psi = 30^\circ$, azimuthal angle $\phi = 35.2^\circ$ with respect to the [001] direction).
position was done as described in Section 2 by means of a least-squares fit of standard spectra to the alloy spectra.

In addition to the chemical composition we also gain information on the structure of the top layer by means of the total ion signal, defined as the integrated peak areas of both the Rh and Pt intensity in the LEIS spectra: owing to the small difference in element sensitivities between the two elements for the scattering angle of $\Theta = 60^\circ$ ($\sim 1\%$), the total ion signal depends only weakly on temperature-induced changes in the top-layer composition, but primarily on the density of scattering centers in the top layer. Hence, keeping the current of the incident ions and the scattering conditions fixed, we have the possibility to monitor temperature-induced changes of the top-layer geometry simultaneously with the chemical composition.

Fig. 5 shows the top-layer composition of the $\text{Pt}_{25}\text{Rh}_{75}(110)$ surface at variable temperature. The starting point for the LEIS measurement was a reproducible surface configuration established by sputtering under well-defined conditions (500 eV Ar$^+$ ions, ion current density 35 nA mm$^{-2}$, incidence angle 45$^\circ$) for a sufficiently long time. At first we heated the sputtered surface to 1100°C (filled diamonds), then varied the surface temperature several times between 1100°C and 300°C (solid lines), and finally cooled to room temperature (open circles). For each annealing step (markers) we held the surface at constant temperature for 5 min to reach a steady state before recording the LEIS spectra (20 s for one LEIS measurement).

Upon heating the sputtered surface to 500°C we observe a significant increase of the Pt concentration up to 65 at. % Pt. Above this temperature the Pt enrichment decreases constantly with temperature, resulting in a Pt concentration of only 48 at. % Pt at 1100°C. Subsequent temperature variations then reveal a reversible change of the composition above 850°C and a hysteresis-like behavior between 500 and 850°C. In this temperature range the upgoing curve (filled markers) is evidently higher than the downgoing curve (open markers). Below 500°C the top-layer concentration saturates at 82 at. % Pt, which is in excellent agreement with the LEED result of 80% obtained in the previous section.

The existence of a hysteresis behavior between 500 and 850°C (Fig. 5) indicates that there is a considerable influence of the previous temperature treatment on the top-layer composition. This behavior could not be explained by a kinetic limitation of surface segregation, because limited segregation would cause a reduced Pt concentration on the upgoing temperature curve, which is in contrast with experiment. Regarding the less enhanced Pt segregation at high temperature (48 at. %), and the absence of reconstruction on the clean Rh(110) surface [35], we have to examine whether the hysteresis might be due to a temperature-induced deconstruction of the missing-row structure at high temperature. The existence of such a deconstruction can be confirmed by looking at the total ion signals that correspond with the energy spectra used for in Fig. 5.

Fig. 6 shows the temperature-dependent total ion signal corresponding to the Pt concentration in Fig. 5, using the same markers for identical surface conditions. With respect to the sputtered
Fig. 6. The total ion signal measured as a function of the annealing temperature. Between 500 and 1100°C there is a significant difference in the total ion signal depending on the previous temperature treatment. On heating a (1 × 2) missing-row structure, we observe a decrease of the total ion signal followed by a rapid increase, whereas cooling from 1100°C results in a continuous reduction of the total ion signal. The overall change of the total ion signal by a factor of two between 500 and 1100°C is attributed to a temperature-induced de- and reconstruction of the missing-row structure known from LEED (the solid lines are a guide for the eye only).

The upgoing part of the total ion signal in Fig. 6 shows a further and unexpected reduction of the atomic density in the topmost layer around 750°C. Following the same arguments as before, this further reduction of the top-layer atomic density might be due to a (1 × 3) micro faceting [22]. The total ion signal measured as a function of the annealing temperature. Between 500 and 1100°C there is a significant difference in the total ion signal depending on the previous temperature treatment. On heating a (1 × 2) missing-row structure, we observe a decrease of the total ion signal followed by a rapid increase, whereas cooling from 1100°C results in a continuous reduction of the total ion signal. The overall change of the total ion signal by a factor of two between 500 and 1100°C is attributed to a temperature-induced de- and reconstruction of the missing-row structure known from LEED (the solid lines are a guide for the eye only).

As the total ion signal is directly correlated with the atomic density in the top layer, we conclude from the doubling of the signal (in Fig. 6), and the existence of a complete missing-row reconstruction at low temperature (after equilibration) that Pt$_{25}$Rh$_{75}$(110) is deconstructed at high temperature (1100°C). The missing-row structure at room temperature was derived by the structure analysis in Section 3.1 and confirmed by an STM study [33]. Consequently, the hysteresis of the composition (in Fig. 5) is mainly due to the structure transition in the temperature range between 500 and 850°C.

The upgoing part of the total ion signal in Fig. 6 shows a further and unexpected reduction of the atomic density in the topmost layer around 750°C. Following the same arguments as before, this further reduction of the top-layer atomic density might be due to a (1 × 3) micro faceting [22] or to a roughening transition [36], both observed on the clean Pt(110) surface. Although no impurities were detected by AES, a small amount of impurity could play a role in stabilizing the hypothetical (1 × 3) structure [37], or could cause a decrease of the ion count rate by shadowing the top layer. Despite the incomplete understanding of details concerning the structural transition around 750°C, it is evident that a rapid deconstruction of the surface between 800 and 900°C takes place, leading to an fcc(110) (1 × 1) surface at high temperature. On the other hand, the rather slow and continuous reduction of the total ion signal during cooling (open squares) can be attributed to a growth of (1 × 2) missing-row domains, which goes hand in hand with the temperature-induced Pt enrichment of the surface.

From a thermodynamic point of view, the Pt$_{25}$Rh$_{75}$(110) surface is an interesting example, where not only the temperature but also the previous temperature treatment has a significant influence on surface composition and structure. The origin of this striking behavior is the energetic advantage for Pt to segregate to the (111) facets of the reconstructed surface, and the circumstance that Pt segregation itself is essential for the (1 × 2) reconstruction, and thus for the formation of the (111) facets. The structural influence on the segregation behavior becomes evident during the structure transition. When heating the (1 × 2) missing-row reconstructed surface, the reconstruction and the Pt enrichment of the surface are retained up to a temperature of about 700°C. At this
temperature the Pt-rich missing-row reconstruction can be seen as a sort of metastable state, where the Pt enrichment is essential for the surface reconstruction and vice versa. However, at such elevated temperatures this metastable state is no longer the energetically favorable one. The sudden deconstruction of the missing-row structure is expressed by the rapid decrease of the Pt concentration (see Fig. 5) and the simultaneous increase of the total ion signal (see Fig. 6). On the other hand, when cooling from 1100°C, the initial structure is an unreconstructed fcc(110) surface, with a comparably lower segregation energy than during heating. Consequently, the structural difference in segregation energy leads to the lower concentration curve until a complete reconstruction is accomplished. This interplay of Pt segregation and reconstruction is similar to the case of PtNi(110), where the formation of a close-packed surface leads to enhanced Pt segregation, and vice versa [38].

4. Summary

The surface structure and composition of Pt$_{25}$Rh$_{75}$(110) has been studied at variable temperature. By LEED $I$–$V$ analysis ($R_p=0.24$) we have revealed a $(1\times2)$ missing-row reconstruction on the equilibrated surface Pt$_{25}$Rh$_{75}$(110) in analogy to the clean Pt(110) $(1\times2)$ surface. The Pt$_{25}$Rh$_{75}$(110) surface consists of Pt-enriched (111) facets, with a significant Pt enrichment of 80 at.% in the topmost layer, and a Rh-enriched site in the third layer (buried by the topmost atoms). The composition and geometry of deeper atomic layers is almost unchanged with respect to the bulk. By temperature-dependent LEIS measurements we revealed a hysteresis behavior of the top-layer composition, which is obviously connected to a temperature-induced de- and reconstruction of the missing-row structure between 500 and 850°C. Pt segregation is found on both the reconstructed and unreconstructed surfaces, but it is evidently more pronounced on the missing-row reconstructed surface. The comparison of LEED and LEIS results in the present work and STM results of Ref. [33] for the top-layer composition of the same Pt$_{25}$Rh$_{75}$(110) crystal gave an excellent agreement with an absolute error less than 2 at.%.

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