Chemically resolved STM on a PtRh(100) surface

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Abstract

Scanning tunnelling microscopy on PtRh(100) (molar bulk composition 1:1) has revealed the possibility of direct determination of the surface structure of this system. During measurements at low tunnelling resistance (< 500 kΩ), the Pt and Rh atoms appear with a clearly observable apparent height difference of more than 20 pm. No long range ordering has been found. Variation of the sample preparation method and comparison of STM and Auger electron spectroscopy measurements led to the conclusions that there is a preferential surface segregation of platinum, that rhodium atoms are the ones with the highest apparent height, and that there is a limited tendency of clustering on the surface. Furthermore, it was found that platinum atoms preferentially populate the step edges on this crystal surface.

Keywords: Alloys; Low index single crystal surfaces; Metallic surfaces; Platinum; Rhodium; Scanning tunneling microscopy; Surface segregation; Surface structure

1. Introduction

The catalytic activity of an alloy sample is strongly influenced by its surface composition and structure. Depending on the mechanism of the reaction on the catalyst surface, either isolated atoms or ensembles are favourable. To investigate a model catalyst like a single crystal surface, scanning tunnelling microscopy (STM) has proven to be a very useful technique. This holds for pure metals as well as for alloys, as has been shown by Schmid et al. [1] some years ago. On a Pt35Ni75(111) surface they found a clear discrimination of ca. 0.3 Å between the two elements at low tunnelling resistance with nickel having the highest apparent height. In this paper an STM study of the Pt50Rh50(100) surface is presented.

Platinum–rhodium is an alloy that is utilised on a large scale as a catalyst: as an industrial catalyst it is used for the production of nitric acid and hydrogen cyanide, but the major application is the three way catalyst (TWC), which is used for the purification of exhaust gases from gasoline fuelled automobiles. The TWC should be active in CO oxidation, hydrocarbon oxidation and selective reduction of NO to N2. However, the surface composition of the PtRh catalyst is not at all constant because of thermally and chemically induced segregation. These effects have been reported by various authors [2–11]. Ren and Tsong [2] investigated the (100) and (111) surfaces of Pt55Rh45 by means of atom probe field ionisation microscopy. They found a platinum enrich-
ment in the first atomic layer of 71% for (111) and 73% for (100) after annealing at 700°C. Depth profile determination showed a considerable Pt depletion in the second atomic layer. In the presence of sulphur, this segregation pattern was reversed, i.e. there was Rh enrichment on the surface. Using the same technique, Sano and Sakurai [3] found about 60% Pt on the Pt$_{44}$Rh$_{56}$(100) surface and 72% Pt on Pt$_{68}$Rh$_{32}$(100) after annealing at 700°C. Furthermore, after annealing at 600°C they found rhodium enrichment. In the presence of sulphur, this segregation pattern was reversed, i.e. there was Rh enrichment on the surface. Using the same technique, Sano and Sakurai [3] found about 60% Pt on the Pt$_{44}$Rh$_{56}$(100) surface and 72% Pt on Pt$_{68}$Rh$_{32}$(100) after annealing at 700°C. Furthermore, after annealing at 600°C they found rhodium enrichment. On polycrystalline samples of various composition Williams and Nelson [4] using ISS, measured Pt enrichment above 530°C, while under approximately the same conditions Sano and Sakurai [3] measured rhodium enrichment on Pt$_{85}$Rh$_{15}$(110). By means of Auger electron spectroscopy (AES), Beck et al. [5] registered a platinum segregation to the top layers above 600°C on Pt$_{10}$Rh$_{90}$(111). They also studied adsorbate-induced segregation and found that above 600°C, oxygen adsorption causes a decrease in the platinum surface concentration and hydrogen an increase. The results with oxygen are a confirmation of the LEED and electron spectroscopy work by Tamura et al. [6] and Hirano et al. [7] on the (100) surface although segregation temperatures are somewhat lower there. A decreasing platinum segregation occurs at annealing above ca. 700°C in vacuum as was concluded by Siera et al. [8] from AES measurements on the (100) and (111) surfaces of a Pt$_{55}$Rh$_{45}$ single crystal. These results were first rationalised by a vibrational entropy model (see e.g. Ref. [9]) in which a surface vibration entropy effect favours a higher platinum concentration on the surface. Later, Legrand and Tréglia [10] applied the tight-binding Ising model to the (100) and (111) surfaces of PtRh. The TBIM is based on differences in surface tensions of Pt and Rh, and satisfactorily explains the platinum surface segregation, which decreases with increasing equilibration temperature [8], by energetic instead of entropic considerations. Brejnak et al. [11] described segregation behaviour in PtRh with the tight-binding–linear muffin tin orbital method and were able to confirm the generally found trend of platinum enrichment of the surface.

An important remark here is, that the segregation behaviour can be significantly altered by kinetic limitations. It was suggested [4] and agreed on [8,11] that under thermodynamic equilibrium, the (100) surface of any PtRh alloy would be enriched in Pt relative to the bulk and that this enrichment would decrease with increasing annealing temperature.

In this study, attempts were made to get chemical resolution on a Pt$_{50}$Rh$_{50}$(100) single crystal surface by means of scanning tunnelling microscopy. Beforehand this was expected to be difficult because of the striking similarity of Pt and Rh concerning atomic radius, thermodynamic features [9,12], and electronic structure near the Fermi level. By statistical analysis, the surface structure and distribution of the two elements over the surface could be derived from the STM images and by comparing to AES results, the chemical nature of the surface atoms could be identified.

2. Experimental procedure

The single crystal surface used in this study, Pt$_{50}$Rh$_{50}$(100), was cleaned in vacuum by annealing cycles running between 600 and 850°C, at the same time sputtering with 1 keV Ar$^+$ ions. This procedure was applied for ca. 80 h resulting in Auger spectra of the crystal surface that were free of Si and C peaks. The presence of a low amount of sulphur can not be excluded because the S Auger peak (152 eV) nearly coincides with one of the Pt Auger peaks. That the lack of this knowledge may be quite unpleasant can be learnt from the theoretical work by Sautet et al. [13,14] and by the suggested explanation of STM results by McIntyre et al. [15], which points out that sulphur may have a beneficial influence on the corrugation.

The scanning tunnelling microscope used in this study was a commercial Omicron micro-STM which has been provided with additional vibration damping: the STM head itself is supported by a viton stack and the entire vacuum chamber has been suspended by a combined spring-elastomer system [16]. Scans were performed with electrochemically etched tungsten tips, which were cleaned in vacuum by Ar sputtering, field evaporation and voltage pulses (up to 10 V). The sample
bias was negative and for recording the highly resolved images shown in this paper, tunnelling voltages of 0.5 mV were applied. During STM measurements, the pressure in the STM chamber was $2 \times 10^{-11}$ mbar. Nevertheless, Auger spectra taken after the STM measurements have shown a small amount of carbon, which is probably due to carbon segregation and possibly some contributions of residual gases. No Auger spectra were taken before the STM measurements to avoid contamination of the surface; consequently, no information is available on the development of the surface composition under the influence of the C segregation at room temperature. The AES measurements were performed using a cylindrical mirror analyser with a coaxial electron gun, producing a beam of 2 keV primary electrons.

3. Results and discussion

A typical STM image with chemical resolution is shown in Fig. 1. Already at first sight there is a clear discrimination between two intensity levels which can be attributed to the two chemical elements present on the surface. In this case, the surface had been prepared for measurement by sputtering followed by annealing at 850°C. According to the literature [8,9] a significant platinum surface segregation was expected and indeed, this was found by AES. After some limited filtering for removing the z drift from the STM image, a histogram of the apparent heights could be made, resulting in the graph shown in Fig. 2. Two nicely separated peaks are visible, with a height difference between the local maxima of ca. 22 pm as was deduced after fitting a double Gauss curve. Using the same analysis the peak area ratio of the two peaks in the histogram was determined to be 0.45. Following the same procedure, the crystal surface was analysed after a somewhat different preparation, namely sputtering, and at the same time running annealing cycles between 600 and 850°C. In that case, the peak area ratio was 0.56.

The difference in surface composition resulting from the different preparation procedures is explained by a too low diffusion constant of the bulk atoms in PtRh in this temperature regime [4]: sputtering and annealing at the same time consequently leads to a Pt surface concentration which is closer to the bulk concentration than in the case of allowing the surface to reach equilibrium. Comparing the Pt$_{64}$/Rh$_{36}$ peak-to-peak ratios from the Auger spectra as taken after recording the STM images indicated a lower Pt surface concentration in the latter case. From this it can be concluded that the atoms forming the high apparent height peak in the histogram should be rhodium, the lower atoms being platinum. Knowing that, the (100) surface composition of this Pt$_{50}$Rh$_{50}$ crystal could easily be calculated. The respective concentrations for the two cases mentioned earlier were Pt$_{68}$Rh$_{32}$ and Pt$_{64}$Rh$_{36}$. Two extra remarks have to be made here. First, it is well known from the work by Tsong et al. [17] that Pt enrichment in the top layer of the (100) and (111) surfaces of PtRh and PtRu is accompanied by Pt depletion in the second layer. This second-layer information is of course convoluted in the AES data of, in this case, the PtRh surface. Second, as is clearly visible in Fig. 1, there is a small amount of a third species present on the surface. In Fig. 2 this can be seen by the small low apparent height shoulder in the histogram between

Fig. 1. Chemical resolution on the Pt$_{50}$Rh$_{50}$(100) surface. Image size is 200 x 200 Å; tunnelling conditions are 0.5 nA at 0.5 mV. Bright spots are rhodium atoms.
20 and 30 pm. This was presumably carbon coming either from residual hydrocarbons in the STM chamber or from carbon segregation from deeper layers of the crystal; this carbon could be detected in the Auger spectra after the STM measurements. This effect masked a certain percentage of the surface; in an earlier STM study on PtNi [18] it has been shown that not only the carbon atom itself, but also the nearest-neighbour metal atoms will have a considerably decreased apparent height, which could account for the dark areas in the STM image. Knowing that the Rh–C bond strength is higher than the Pt–C bond strength, it could well be that this contributes to disturbances of a few percent in the surface composition as determined by analysing the STM images.

The difference between the apparent heights of Pt and Rh found in the STM data cannot be explained by the difference of the atomic radii (4 pm) or by different geometric height, i.e. the difference of relaxation between Pt and Rh. Since the chemical resolution on PtRh does not require unusual tip conditions (such as an adsorbate on the tip) as needed for chemical resolution on PtNi(111) [1], it must be assumed that the chemical contrast is due to the different electronic structures of Pt and Rh which, unlike Pt and Ni, are not in the same column of the Periodic Table.

During the measurements it was possible to image the step edges of a big terrace, an illustration of which is shown in Fig. 3. The striking fact is that the step edges seem to be almost entirely populated by platinum atoms, which is an interesting phenomenon from a physical as well as a catalytic point of view. Schoeb et al. [19] calculated the population at the step edges of a PtRh cluster of 201 atoms. Their results predict that 82% of all edge atoms of Pt0.5Rh0.5 would be platinum, which nicely agrees with the edge population in Fig. 3 of this paper.

From the well-resolved images, the ordering of the elements at the surface could be deduced. Using image processing techniques, the correlations between neighbouring atoms were calculated from
Fig. 3. Image of a step edge on the Pt$_{0.5}$Rh$_{0.5}$(100) surface. Image size is 200 $\times$ 200 Å; tunnelling conditions are 0.5 nA at 0.5 mV. As the dark species were found to be Pt atoms, it can be concluded that mainly Pt atoms populate the step.

the STM image (Table 1). The data show a positive correlation between nearest (i.e. in the [011] and [01i] directions) and next-nearest neighbours, indicating a limited amount of clustering. The small negative correlation of third and fourth nearest neighbours is due to the small cluster size. Correlations of further neighbours ($n > 4$) are indistinguishable from noise.

The degree of ordering and mixing in PtRh has been subject to some discussion. On the basis of classical tight-binding d-band theories, PtRh would be predicted to separate in two phases [20,21] at low and ambient temperatures, which agrees with extrapolations by Raub [22], based on the observation of a miscibility gap in the phase diagrams of PdIr, PtIr and PdRh. Nevertheless, there has never been any experimental evidence for this phase separation except in a recent paper by Lakis et al. [23]. These authors reported the presence of a low T miscibility gap for small PtRh particles (<10 nm) on Al$_2$O$_3$. From first-principle quantum mechanical calculations, not using the tight-binding approximation, PtRh has been predicted not to separate into phases but rather to order [24]. For low temperatures a long range ordering tendency is found with the highest stability for the ordering with I$_{4}$_1/amd symmetry (Schoenflies D$_{4h}$, “40” as proposed in Ref. [25]); at higher temperatures, indications of a short range ordering were deduced. Analogous to the situation with PtNi [1], a surface ordering of PtRh should be expected as a result of this bulk ordering. However, a limited degree of clustering was registered in our study, an observation which could as well be more consistent with a low T miscibility gap in the phase diagram of PtRh. In this context it should be noted that, most probably, the top and second layers of our PtRh crystal are in thermodynamic equilibrium with each other, but not in equilibrium with the bulk [9].

4. Conclusions

In this article, the ability of STM to image a PtRh alloy surface with atomic resolution is shown. In addition, the component Pt and Rh atoms could be distinguished. In agreement with literature data, the results show Pt surface enrichment on the flat terraces. Furthermore, it was shown that Pt and Rh form small Pt clusters and Rh clusters. Step edges could be imaged and were found to consist mainly of Pt atoms.

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