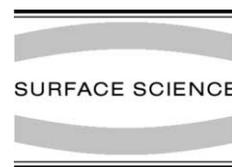




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# Rh/Al bimetallic system with different thickness of Rh layer—AES characterisation and CO oxidation

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## Abstract

CO oxidation over Rh/Al bimetallic system was studied by method of molecular beams (MBs). Rh films were evaporated in situ onto Al polycrystalline substrate. The samples with different amounts of deposited rhodium were prepared. Sample purity and composition were checked by Auger electron spectroscopy and electron energy loss spectroscopy. Rh–Al alloy forms on the sample surface during annealing of this system. CO oxidation was investigated in steady-state experiment using two separated MBs of CO and O<sub>2</sub>. Experiments were performed in a dynamic mode (linear increase and decrease of the sample temperature to study the hysteresis effects). The influence of Rh layer thickness as well as of CO and O<sub>2</sub> MB intensity ratio on the CO<sub>2</sub> production was studied. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Rhodium; Aluminum; Carbon monoxide; Oxygen; Surface chemical reaction; Oxidation; Auger electron spectroscopy; Alloys

## 1. Introduction

Catalytic oxidation of CO is an effect of a great scientific interest and it plays an important role, e.g. in air pollution control. Most of the heterogeneous catalysts in industrial processes are multi-component systems. Adsorption studies on alloy surfaces with different composition may contribute to the understanding of some of these processes. Alloying metals change their geometrical and electronic structure, and, as a consequence, also their interaction with adsorbed species [1].

Within this paper, we have studied the CO oxidation on Rh layers of various thickness deposited onto Al polycrystalline substrates. Molecular beam (MB) technique has been used in these experiments, because it is a suitable method for investigation of a wide range of kinetic processes related to the surface reactions [2,3]. The dependence of the CO<sub>2</sub> production on the average Rh layer thickness has been discussed.

## 2. Experimental

Experiments were carried out in an ion-pumped UHV system with a base pressure better than  $2 \times 10^{-8}$  Pa, equipped with a specially designed spectrometer which has been described previously [4]. CO and O<sub>2</sub> exposures were performed simultaneously by means of a MB doser facing the sample

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surface. The intensity of the mixed beam was about  $1.5 \times 10^{13}$  molecules/cm<sup>2</sup> at the sample surface. Three ratios of CO and O<sub>2</sub> partial pressures have been used –1:1, 2:1 and 1:2. The total pressure in the vacuum chamber during the scattering experiments was  $1 \times 10^{-6}$  Pa. The scattered or desorbed molecules were monitored by the quadrupole mass spectrometer (QMS) Leybold Inficon 2000. It was positioned in a differentially pumped chamber with a small entrance orifice. The sample was positioned in proximity to this orifice, in order to examine small surface area where the surface temperature distribution could be considered as homogeneous. The temperature was determined by a chromel–alumel thermocouple fixed on the sample holder.

A double-pass cylindrical mirror analyser DESA 100 equipped with an electron gun (Steib Instruments) was used for Auger electron spectroscopy (AES) and electron energy loss spectroscopy (EELS) measurements. The primary energy of an electron beam was 2.5 keV. Measured AES intensities were normalised to a reference Rh foil peak intensity. The energy of the Auger Rh (M<sub>45</sub>N<sub>45</sub>N<sub>45</sub>) peak measured on the reference foil was equal to  $297.3 \pm 0.3$  eV during all AES experiments.

The Al samples were prepared from Goodfellow materials (GFM) 99.999% Al cut into a plate of  $10 \times 10$  mm<sup>2</sup> area and 1 mm thick. The chemical etching followed the sample polishing. Details of these procedures are given in [5]. Inside the vacuum chamber, substrates were sputtered by Ar<sup>+</sup> ions (incident energy 2 keV, ion current density at the sample  $5 \times 10^{-7}$  A/cm<sup>2</sup>, 60 min). After that, annealing at 770 K for 10 min followed and the ion sputtering with the same parameters has been performed again. After this procedure, the aluminium Auger peaks exhibited only a metal form, no chemical shift of the peak was observed. Neither carbon nor oxygen signal was detected.

Rhodium was evaporated at a room temperature from the micro electron beam evaporation source (MEBES) [6]. In this evaporation cell, a GFM 99.9% Rh wire was evaporated by the high voltage accelerated electrons. Evaporating rates were estimated by a quartz thickness monitor

(QTM). The evaporation rate stability during the long evaporation time was ensured by the measurement of the evaporated ion current [5].

Immediately after evaporation, samples were annealed at 630 K for 10 min. There were two main reasons of the annealing. Firstly, temperature stimulated alloying of Rh and Al was expected [5]. Secondly, samples were stabilised preliminary to following reactive scattering experiments. Within these experiments, samples were heated at 570 K maximally. Annealing of samples at higher temperature than 630 K leads to the significant incorporating of Rh layer into Al substrate [5].

Reactive scattering experiments started at room temperature. The sample was placed into the mixed beam of CO and O<sub>2</sub> and after that the temperature rose gradually to 570 K and dropped back to the room temperature again. Mass spectra of scattered and/or desorbed species were collected during this temperature treatment. This annealing–cooling cycle was repeated several times to ensure the stability of investigated effects. The rate of temperature variation was held at 0.25 K/s. During the first annealing–cooling cycle, the sample was oxidised significantly due to impinging oxygen. With regard to the AES results, we assume this oxidation applies to the Al component only. After finishing experiments, samples were taken from the vacuum chamber and they were analysed by electron micro probe (EMP).

The reference Rh sample was GFM 99.9% Rh  $10 \times 10 \times 0.125$  mm. It was sputtered by Ar<sup>+</sup> ions (incident energy 1 keV, ion current density at the sample  $10^{-6}$  A/cm<sup>2</sup>, 15 min). After that, annealing at 770 K for 20 min in oxygen atmosphere followed.

### 3. Results and discussion

Parameters characterising deposited samples are given in Table 1. This table contains a comparison between the Rh layer thickness estimated by QTM and EMP techniques. For EMP, it should be noted the measured thickness was close to the resolving power of this technique. In the following text, the thickness estimated by QTM will be used instead. The last column of Table 1 contains

Table 1  
Parameters characterising deposited samples

| Sample | Rh thickness (QTM) (nm) | Rh thickness (EMP) (nm) | Al oxide thickness (EMP) (nm) |
|--------|-------------------------|-------------------------|-------------------------------|
| 1      | 0.3                     | 0.5                     | 2.1                           |
| 2      | 0.6                     | 1.3                     | 2.0                           |
| 3      | 1.0                     | 1.6                     | 1.9                           |
| 4      | 2.0                     | 2.5                     | 1.9                           |

aluminium oxide thickness estimated by EMP. Obviously, the values are the same for all samples. This fact will be remarked below in context of AES and EELS results. For the Rh layer thickness determined by EMP, it should be noted that the values were measured assuming the Rh bulk material density. For our annealed samples, the real density is lower due to Rh–Al alloying. So the real thickness of Rh layer dispersed in Al is higher than values in Table 1.

### 3.1. AES and EELS results

The general behaviour of AES spectra measured on Rh/Al bimetallic system during sample heating and oxidation has been published previously [5]. In this paper, we will append some results related to reaction scattering experiments.

Measured AES  $\text{Al}(L_{23}M_1M_{23})$  and  $\text{Rh}(M_{45}N_{45})$  peaks are plotted in Figs. 1 and 2. It is clear that Al signal disappears as a consequence of increasing Rh layer thickness (Fig. 1b and c). The peak at  $\approx 37$  eV arises simultaneously with this disappearing. Obviously, this peak can be adjudged to Rh layer [7]. As a consequence of Rh layer annealing, the Rh–Al alloy forms and Al spectrum changes remarkably. It becomes very similar to the spectrum measured on clean Al substrate (Fig. 1d). Reactive scattering experiments are shown to cause a marked oxidation of the sample (Fig. 1e). We are not surprised at this behaviour because of our observation of Al disposition to oxidation in an impinging oxygen beam.

$\text{Rh}(M_{45}N_{45})$  energy measured on Rh foil (Fig. 2a) equals to 297.5 eV. The energy of the same peak measured on 0.3 nm thick Rh layer on Al substrate (Fig. 2b) equals to 295.5 eV. The shift is caused by a bimetallic interaction between Rh

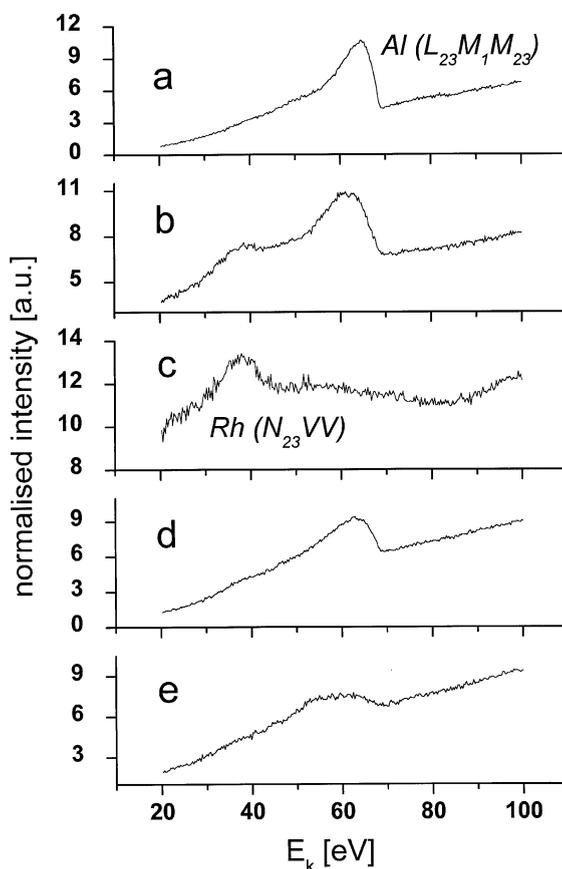


Fig. 1.  $\text{Al}(L_{23}M_1M_{23})$  Auger peak development in dependence on Rh layer thickness and on the temperature treatment of the sample: (a) clean Al substrate, (b) 0.3 nm of Rh evaporated (sample 1), (c) 2.0 nm of Rh evaporated (sample 4), (d) after 10 min annealing of 2.0 nm thick Rh layer at 630 K (sample 4), (e) the same sample after reaction scattering experiments.

and Al. As the thickness of Rh layer increases, this interaction becomes less responsible for the AES Rh peak position and the peak energy shifts back to the bulk value, accompanied with an increase of the peak intensity (Fig. 2c). As a result of sample annealing, Rh layer forms an alloy with Al substrate [5] and bimetallic interaction becomes responsible for AES Rh peak position again, accompanied with a well-marked decrease of the peak intensity and the change of the peak shape as well (Fig. 2d). Reactive scattering experiments do not seem to influence the peak position and intensity (Fig. 2e). It should be noted that Al as well

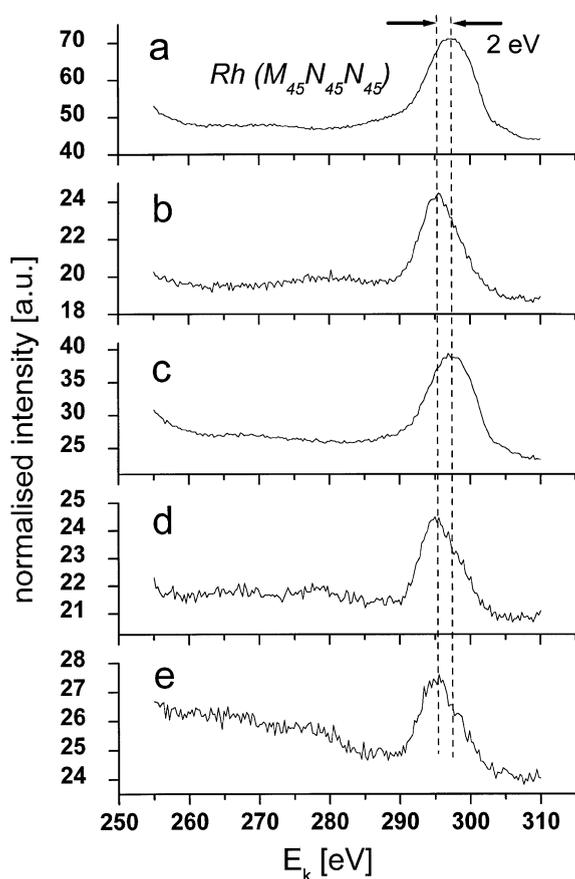


Fig. 2. Rh(M<sub>45</sub>N<sub>45</sub>N<sub>45</sub>) Auger spectra development in dependence on Rh layer thickness and on the temperature treatment of the sample: (a) clean Rh foil, (b) 0.3 nm of Rh evaporated on clean Al substrate (sample 1), (c) 2.0 nm of Rh evaporated on clean Al substrate (sample 4), (d) after 10 min annealing of 2.0 nm thick Rh layer at 630 K (sample 4), and (e) the same sample after reaction scattering experiments.

as Rh peaks measured after the annealing of the sample and after the reactive scattering experiments were identical at all samples.

Oxygen (KL<sub>1</sub>L<sub>1</sub>) peak appeared markedly as a result of Al oxidation during reactive scattering experiments. All the same, the intensity of this peak was uniform for all samples. Since all of monitored AES peaks show this behaviour, we conclude that the surface structure (in the significance of AES information depth) of the sample does not depend upon Rh layer thickness (see Table 1) after the annealing and after the reactive

scattering experiments. This conclusion is well supported by the EMP results for aluminium oxide thickness (see Table 1). The main conclusions from EELS results collected on Rh/Al system will be published in a separate paper soon. Shortly, the spectra taken at all samples after the annealing and reactive scattering experiments were identical. There was a dependence upon primary energy of the electron beam, of course. We have used three primary energy values: 300, 500 and 1000 eV. The EELS results are explicitly conformable with AES and EMP results for oxide thickness as well.

### 3.2. Results of reactive scattering experiments

Comparison of a temperature dependent CO<sub>2</sub> production on sample 3 and reference Rh foil is presented in Fig. 3. The background of the residual gas pressure in the vacuum system has been subtracted. The development of CO<sub>2</sub> signal for the rising and decreasing temperature is different. It shows a significant hysteresis, which is neither “clockwise”, nor “anticlockwise” (Fig. 3). The main difference between sample 3 (Fig. 3a) and Rh foil (Fig. 3b) is in the intensity of CO<sub>2</sub> signal. This is due to the much lower Rh surface concentration on sample 3 (see Section 3.1). Important features of curves in Fig. 3 are the position and the intensity of maximum during the temperature increase and the variation of these parameters measured during the temperature decrease. At all Rh deposited samples (Table 1), these parameters were identical in limits of the measurement precision, given by the accuracy of reading data plotted in Fig. 3 (the position of rate maximum was determined with the accuracy ≈30 K). That is why only data for sample 3 are plotted in Fig. 3. These general features of hysteresis loops were reproduced several times, in experiments one after the other, with ≈40 min duration each.

The shape of curves measured on sample 3 (Fig. 3a) is very similar to that one measured on Rh foil. So we can assume essentially the same reaction mechanism in both cases. The maximum intensity of CO<sub>2</sub> signal appears at lower temperature for Rh foil (Fig. 3b). This fact could be related to the greatly higher adsorption capacity of Rh foil.

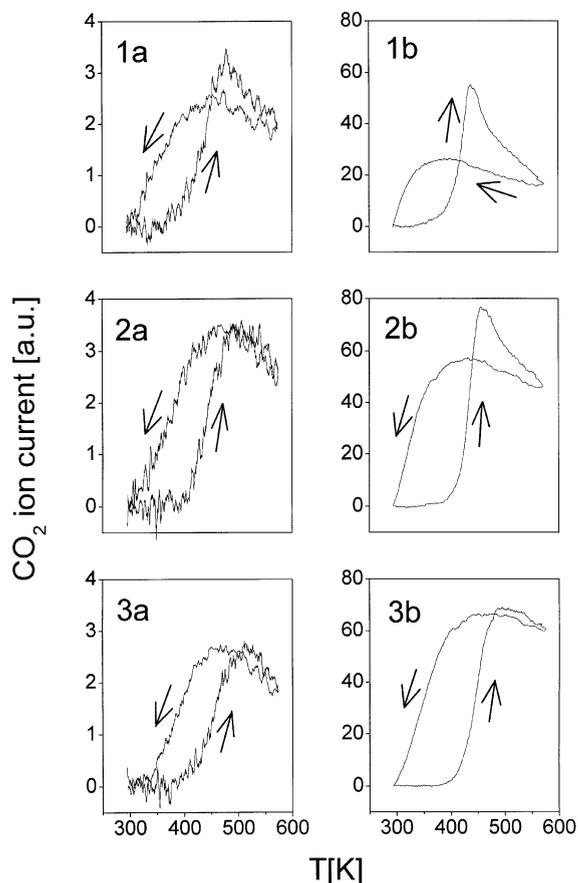


Fig. 3. CO<sub>2</sub> production on sample 3 and Rh foil: behaviour of CO<sub>2</sub> ion current. Pictures marked (a) belong to sample 3, pictures marked (b) belong to Rh foil. The numbers indicate the ratio of CO and O<sub>2</sub> partial pressures: 1...1:2, 2...1:1, 3...2:1. Arrows point in the right direction of hysteresis loops.

Surface concentrations of adsorbed CO and O<sub>2</sub> are important rate-determining factors. At low temperature, CO inhibits adsorption of oxygen [8], so the reaction rate is low. As the temperature increases, the CO concentration decreases which enables the more intensive adsorption of oxygen and the reaction rate increases. After reaching the maximum reaction rate, the CO concentration decrease continues and it lowers the rate. The temperature of this maximum is lower for Rh foil due to less pronounced CO inhibition of oxygen adsorption positions in a MB of a given intensity. As a result of MB intensity increase, the differences

in temperature of maximum reaction rate should diminish. We were not able to increase this intensity due to experimental limitations.

It should be noted that the used methods do not give any detail information on the type of CO adsorption, see e.g. [9,10]. For Rh foil, molecular as well as dissociative adsorption has been observed [11]. That is why measured hysteresis loops will be discussed in more detail elsewhere.

#### 4. Conclusions

The catalytic activity of Rh/Al bimetallic system towards CO oxidation has been investigated. It has been shown that the surface structure as well as reactivity does not depend upon Rh layer thickness in a range between 0.3 and 2.0 nm. The maximum reaction rate as well as Rh surface concentration were approximately ten times lower compare to Rh foil values. The reaction mechanism is probably the same as it is on Rh foil.

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