SEGREGATION OF BORON AND ITS REACTION WITH OXYGEN ON Rh

János KISS, Károly RÉVÉSZ and Frigyes SOLYMOSI

Reaction Kinetics Research Group of the Hungarian Academy of Sciences
and
Institute of Solid State and Radiochemistry, University of Szeged, P.O. Box 105, H-6701 Szeged, Hungary

The segregation of boron and its reactivity towards oxygen has been investigated by means of AES, XPS, UPS and ELS (in the electronic range) in the temperature range 100–1300 K. The segregation of boron in a Rh foil started from 700 K. The segregated boron produced a peak in XPS for the B(1s) level at 187.8 eV and emissions in UPS at 4.0 and 8.6–9.0 eV for B(2p) and B($2sp^2$), respectively. Analysis of the results suggested that the segregated boron on Rh foil mainly forms dimers or islands, instead of isolated monomers, without any significant charge transfer between rhodium and boron. Upon oxygen adsorption the B(1s) and O(1s) levels shifted to higher binding energy (to 191.5 and 532.6 eV, respectively) and a new loss in the EELS was produced at 9.4 eV, demonstrating a strong chemical interaction between oxygen and boron. The interaction occurs at as low as 159 K, as indicated by the development of the 9.4 eV loss feature. It is assumed that boron suboxides are formed in which the B–B bond is retained. The cleavage of the B–B bond starts above 400 K and is completed at 750 K, when the $2sp^2$ hybrid state at 8.6–9.0 eV in the UPS, due to the B–B bond, is no longer detected. Formation of a polymer-like B_2O_3 species is proposed which reacts with elemental boron above 900 K to give B_2O_2.

1. Introduction

The presence of adatoms (either as impurities or promoters) on metal surfaces can drastically influence the surface reactivity; this is in most cases attributed to an electronic interaction between the adatoms and the metals. However, there is increasing evidence that surface adatoms can interact directly with gaseous molecules, thereby strongly influencing the reactivity [1].

We recently demonstrated that boron impurity segregating to a Rh surface dramatically alters the reactivity of the Rh surface towards N- and O-containing moieties, such as CN [2], NO [3], CO_2 [4] and H_2O [5]. A possible reason for this phenomenon is that boron forms very strong bonds with N and O, which can promote the processes of surface dissociation of the adsorbed molecules. Following surface dissociation, we detected the formation of dissociation products via thermal desorption, and a new feature at 9.4 and 7.2 eV

in the electronic electron energy loss spectrum. These losses were tentatively attributed to the formation of a B–O and B–N surface species. The segregation of boron onto a Rh surface has also been observed by other authors [6–9].

In the present work we examine the segregation of boron and the interaction of segregated boron with oxygen by means of different electron spectroscopic methods, such as AES, XPS, UPS and ELS (in the electronic range). The primary aims were to determine the effects of oxygen on the segregation process, to evaluate the nature of the interaction and the surface products formed.

2. Experimental

The experiments were performed in an ultra-high vacuum system, with a background pressure in the low-to-middle 10^{-10} Torr range, produced by turbomolecular and titanium getter pumps. The system was equipped with a hemispherical analyzer (Leybold–Heraeus LHS-10) for UPS, XPS and AES, a CMA (PHI) for EELS, an Ar ion gun for cleaning and a quadrupole residual gas analyzer.

UPS was performed by using He I (21.22 eV) and He II (40.81 eV) radiation. The angles between the surface normal and the UV lamp and between the surface normal and the analyzer were 75° and 16°, respectively. Spectra were taken in 5–10 min. Work function measurements were obtained from He I spectra, by using the energy difference between the photoelectron secondary onset and the Fermi edge (with the sample biased negatively). The photoelectrons were excited by Al Kα radiation (1486.7 eV) in the XPS regime. The energies of the XPS peaks were calibrated relative to the Fermi level of Rh. The peaks were measured by using a pass energy of 50 eV in order to get the optimum resolution by maintaining an acceptable signal-to-noise ratio at measuring times of 30–60 min.

The experimental data (UPS and XPS) were collected for further work-up with a multichannel analyzer (Tracor-Northern 1710) and a computer.

High resolution Auger electron spectra were taken in $dN(E)/dE$ mode using a lock-in amplifier (Itacho, Dinatrac 391 A) with 0.5–2 eV peak-to-peak modulation, 0.2–1 μA of incident current and 2.5 kV of incident energy.

For electron energy loss spectra the gun of a CMA was used as a primary electron source with an energy of 70.0 eV and a beam current of 0.1–1.0 μA. The backscattered electrons were analyzed with the CMA. A modulation voltage of 0.1 eV was found to be the optimum for the system used. The speed of taking a spectrum was varied between 0.4 and 4.0 eV/s. The exact positions of the peak maxima of energy losses were determined by a Keithley electrometer. Electron energy loss spectra were taken in $dN(E)/dE$ form.

The polycrystalline Rh foil (10 × 10 mm and 0.127 mm thick 99% purity) was purchased from Hicol Co. The detailed cleaning procedure of the sample has been described elsewhere [4,5]. It consists of cycles of oxygen treatment, ion bombardment and annealing. Segregation of boron was achieved by annealing the Rh foil at 750–1200 K.

3. Results

3.1. Segregation of boron to a Rh surface

The segregation of boron was investigated by means of AES, XPS, UPS, $\Delta\phi$ and ELS (in the electronic range) in the temperature range 300–1170 K.

The boron level on the surface was characterized by computing the ratio of the peak-to-peak heights of the B(KLL) to the Rh (302.0 eV) transition in the Auger electron spectrum. The minimum of this ratio, henceforth called R_B, the B/Rh ratio, for brevity, is about 0.003 and corresponds to "clean" Rh foil. When the freshly sputtered surface was heated to above 700 K, this ratio increased with the temperature up to 980–1000 K and remained constant, $R_B \approx 0.07$, up to 1270 K (fig. 1). (Experiments cannot be extended to higher temperatures because of the construction of our sample holder.)

Boron coverages were calculated by using the ratio of the theoretical XPS photoionization cross-sections [10] for adsorbed boron and oxygen and comparing to the XPS signal from the known oxygen coverage on polycrystalline Rh at saturation [11] (5.8×10^{14} O atoms/cm²). In this way we found 5.8×10^{14} B atoms/cm² at the highest boron concentration, which is about a half of a monolayer. This value corresponds to a relative Auger peak ratio of $R_B \approx 0.075$.
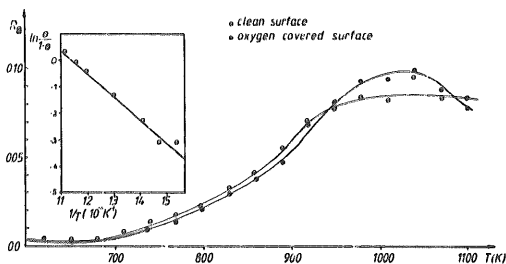

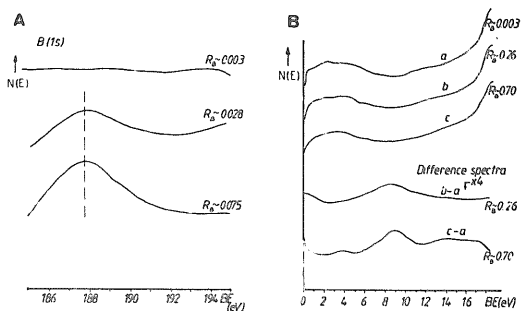Fig. 1. Plot of the B/Rh Auger peak ratio (R_B) versus temperature.

Fig. 2. (A) XP spectra of B(1s) level, (B) UP spectra for boron-containing Rh foil.

The segregation of boron was evaluated with the Langmuir–McLean equation (assuming that the segregation process is in equilibrium in this temperature range):

$$\theta / 1 - \theta = \chi \exp\left(E_{seg} / RT \right),$$

where $\theta = R_B / R_B^{max}$ is the ratio of the Auger peak amplitudes of boron, χ is the bulk concentration of boron, E_{seg} is the energy of segregation of boron to the Rh surface, and R and T are the gas constant and absolute temperature. From the plot shown in a segment of fig. 1, a segregation energy of −71.5 kJ/mol was calculated.

The segregation of boron was also followed by monitoring the B(1s) level as the surface was heated in a stepwise fashion. In the XPS, the segregated boron produced a very broad peak for the 1s level at 187.8 eV at low and at high surface concentrations (fig. 2A). Its intensity increased with the boron concentration.

Fig. 2B shows UP spectra of clean and boron-containing Rh surfaces. As expected, the Rh(3d) band is attenuated with increasing boron coverage. Emission from the B(2p) derived state (at 4.0–5.0 eV below the Fermi level) could just be established. Magnified difference spectra show a peak at 8.6–9.0 eV, the intensity of which increased slightly with the boron coverage. This feature could be due to the adsorption of residual gases, but the XPS and AES did not reveal any detectable surface contamination. Therefore, this peak is tentatively attributed to emission from the $2sp^2$ hybrid state [12].

3.2. Effects of oxygen

In the subsequent measurements we examined the effects of preadsorbed oxygen on the segregation of boron, and the nature of the interaction of oxygen with the boron-contaminated surface.

3.2.1. AES studies

The clean Rh foil was saturated with oxygen at 300 K, then heated up in a stepwise manner to high temperature, and the changes in the AES were monitored. The data in fig. 1 show that the boron starts to segregate at 700 K, similarly as in the case of the clean surface. Above 950 K, however, more boron segregates to the surface. Above 1050 K, the intensity of the boron signal starts to decrease, and it reaches the value for an oxygen-free surface, indicating that a strong interaction occurs between oxygen and boron.

Further measurements showed that in the presence of boron the oxygen uptake increased slightly at 300 K. At $R_B = 0.075$, the amount of adsorbed oxygen was 1.3 times higher than on clean Rh foil. The sticking probability on clean polycrystalline Rh at 300 K was calculated to be 0.33 (in harmony with the earlier data obtained for polycrystalline Rh [11]), and the corresponding value at $R_B \approx 0.075$ was 0.69.

The interaction of oxygen with clean and with boron-containing Rh surfaces was investigated by means of high-resolution AES. The spectrum of a Rh surface cleaned by ion bombardment and by annealing at 700 K exhibits only signals due to Rh. By careful examination of the boron energy region at 160–185 eV, we could detect only a break or shoulder at 170–185 eV (fig. 3a). These features were practically always present in the AES of clean Rh samples. When the sample was heated above 700 K (allowing the segregation of boron), a very intense asymmetric peak developed, with peak maxima at 178–182 eV (fig. 3b).

When the boron-containing Rh surface ($R_B \approx 0.07$) was exposed to oxygen at 300 K, the boron Auger fine structure drastically changed (fig. 3c). A new signal appeared at 171 eV and two smaller ones were detected at 158 and 185 eV. These spectral changes were observed even at low oxygen exposure. The structure of the spectrum remained practically the same up to 700 K, but above this temperature the feature of elementary boron developed gradually.

The adsorption of oxygen on clean Rh resulted in a main peak for the oxygen KLL transition at 518 eV (fig. 4). The position of this peak did not change with exposure and heat treatment up to 700–750 K.

On the boron-containing Rh surface ($R_B \approx 0.07$), oxygen adsorption at low oxygen exposure produced a peak at 513 eV. With increase of the exposure, the intensity of this peak increased, but in parallel with this change a new peak developed at 518 eV (fig. 4). With increase of the temperature, the intensity of the peak at 518 eV decreased and a slight intensification of the feature at 513
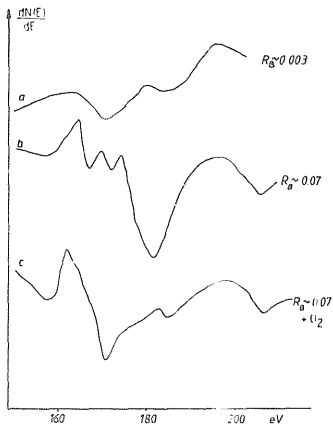
Fig. 3. High resolution Auger spectra in the range of boron transitions: (a) clean Rh foil, (b) after heating the surface to 1000 K, (c) boron-containing surface exposed to 4 L O_2 at 300 K.
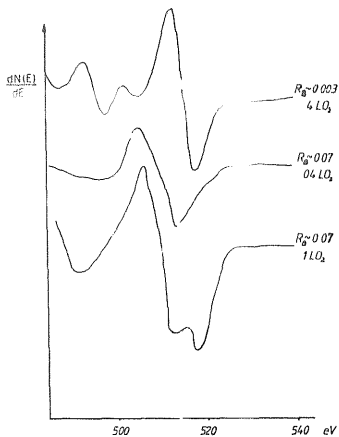

Fig. 4. Oxygen Auger line shape after adsorption of oxygen on clean and boron containing Rh foil at 300 K.

eV was observed. The oxygen Auger signal at 513 eV decreased from 900 K on, but traces of surface oxygen were detected even at 1100 K; this could be eliminated only by prolonged heat treatment at 1100 K or by Ar$^+$ bombardment.

3.2.2. EELS studies

Although dioxygen readily dissociates on the Rh(111) surface at 300 K and yields an intense signal at 518–520 eV in the AES it produced no new loss feature at either 110 or 300 K in the EELS of a clean Rh(111) surface [4,5]. The only observable change was an intensification of the elastic peak and the intrinsic loss of Rh at 5–6 eV. There was no sign of the development of a new loss, even after heating of the oxygen-covered surface up to 1300 K. In the temperature range 110–643 K, the same behavior was found for the cleanest Rh foil, $R_b = 0.003$ (fig. 5). However, above 700 K a new feature developed at 9.4 eV; its intensity first increased, then decreased with the rise of the temperature.

The behavior of boron-contaminated Rh foil ($R_b \approx 0.05$) was completely different. As can be seen in fig. 5, following the adsorption of oxygen at 110 K and after subsequent heating of the sample to higher temperatures, a loss feature at 9.4 eV was produced at around 200 K in the EELS of Rh foil. The intensity of this loss increased up to 650 K and then gradually decreased and it
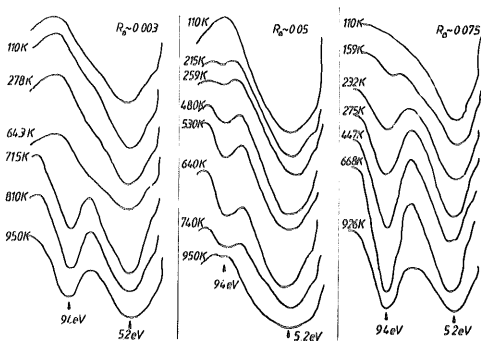
Fig. 5. EEL spectra of Rh foil after heating the samples exposed to 17 L O_2 at 110 K to different temperatures.
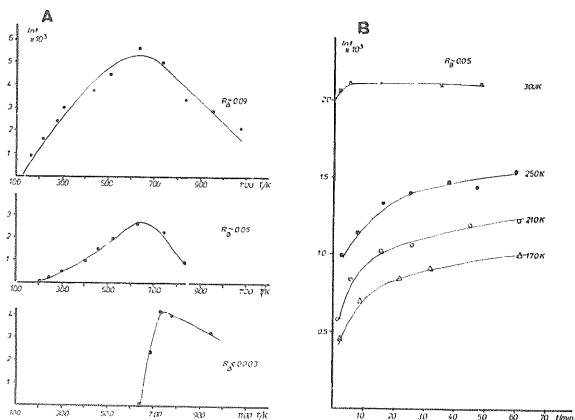
Fig. 6. (A) Changes in the intensity of the 9.4 eV loss following O_2 adsorption on Rh foil at 110 K at different initial boron concentrations. (B) Changes in the intensity of the 9.4 eV loss following O_2 adsorption at different temperatures with time.

disappeared at 950 K (fig. 5). When the surface boron concentration was higher ($R_B \approx 0.075$), the 9.4 eV loss was identified even at 159 K. The intensity of this feature increased up to about 662 K, but the loss was well detectable at 926 K, too.

The effect of temperature on the development of the 9.4 eV loss at different boron concentrations is demonstrated in fig. 6, where the intensity of the 9.4 eV loss (normalized to the elastic peak) is plotted against temperature.

In the subsequent measurements, the time-dependence of the 9.4 eV loss was determined at different temperatures at $R_B \approx 0.05$. In all these cases the surfaces were exposed to 17 L O_2 at a given temperature. The results are presented in fig. 6B.

It is seen that a well observable increase in the intensity of the 9.4 eV loss occurred after a long period even at 170 K, the extent of which was greater at higher temperatures. When the adsorption of O_2 was performed at 300 K, we experienced very little intensity changes after 2 min. The intensity obtained approached the maximum value observed following heating of the sample to 650 K after adsorption at 110 K (fig. 6).
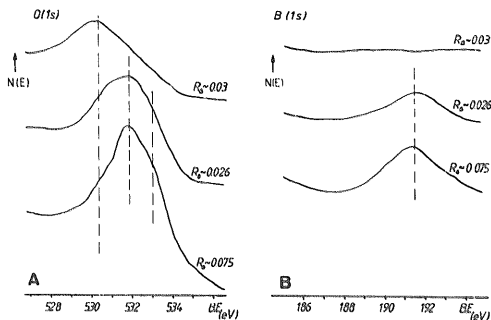
Fig. 7. XP spectra for O(1s) (A) and B(1s) levels (B) after adsorption of 6 L. O_2 at 300 K as a function of boron level.

3.3.3. XPS studies

Fig. 7A shows the XPS for the O(1s) level following the adsorption of oxygen on Rh foil at different boron levels. The adsorption of oxygen on the boron-free surface produced a peak at 530.2 eV. In the presence of boron, the intensity of the O(1s) peak was increased, indicating that the sticking coefficient is higher in these cases. The O(1s) peak at $R_B \approx 0.026$ (corresponding to 2.0×10^{14} boron atoms/cm^2) shifted significantly to higher binding energy (531.8 eV). At the highest boron level of $R_B \approx 0.075$ (corresponding to 5.8×10^{14} atoms/cm^2) the O(1s) peak also appeared at 531.8 eV, but in addition two shoulders were detected, at 530.2 and 532.6 eV.

A large shift to higher binding energy was observed in the B(1s) level, which was independent of the surface boron concentration (fig. 7B). Before oxygen adsorption the B(1s) level appeared at 187.8 eV (fig. 2A), while after the adsorption of oxygen the peak was observed at 191.5 eV.

When the coadsorbed layer was heated to higher temperatures, further shifts in the positions of the O(1s) peaks were observed; the areas of the observed B(1s) and O(1s) peaks, however, did not change up to 950–1000 K. The shoulder in the O(1s) peak at 530.2 eV (adsorbed oxygen on clean Rh) disappeared at about 400 K. The O(1s) peak at 532.6 eV became dominant from 472 K (fig. 8A).

The position of the B(1s) level remained constant up to about 720 K. Above this temperature, the signal shifted to an energy higher by 0.9 eV, indicating further changes in its electron level. From 950 K, the elemental boron feature at 187.8 eV reappeared, when the peak at 192.4 eV vanished (fig. 8B).
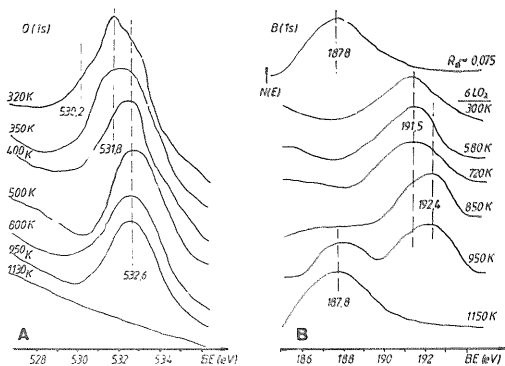
Fig. 8. XP spectra for O(1s) (A) and B(1s) levels (B) after heating the sample ($R_B \approx 0.075$) exposed to 6 L O_2 at 300 K to different temperatures.
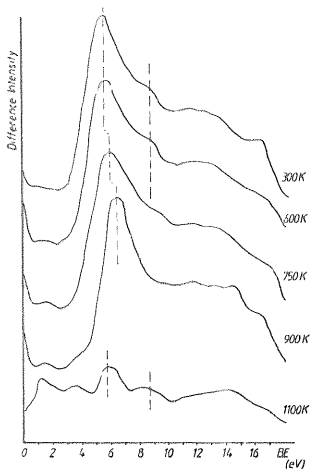

Fig. 9. UP spectra of boron-containing Rh foil ($R_B \approx 0.075$) after heating the sample exposed to 6 L O_2 at 300 K to different temperatures.

3.3.4. UPS studies

The adsorption of oxygen on clean Rh produces O(2p) emission in the He II UP spectrum at 5.5 eV [13]. When boron-contaminated Rh was exposed to a small amount of oxygen at 300 K, the photoemission peak developed in the difference spectrum at 5.9 eV; its intensity increased with the exposure. Emission at 8.6–9.0 eV, tentatively assigned to $B(2sp^2)$, also appeared (fig. 9). When the oxygen saturated surface was heated to higher temperature, the O(2p) level shifted to higher energies (6.4 eV) from 600 K, above which temperature the $B(2sp^2)$ level disappeared. Above 900 K, the intensity of the O(2p) level drastically decreased and the emission at 8.6–9.0 eV for $B(2sp^2)$ was renewed, indicating the development of an elemental boron feature.

4. Discussion

4.1. Segregation of boron to a Rh surface

It has been observed that boron is a major bulk impurity (17 ppm) in Rh [2–9] as a result of heat treatment, the boron segregates to the surface. On the Rh(100) face, the segregated boron forms a (3 × 1) LEED pattern and, as boron is depleted from the bulk, it then segregates to a lesser extent and forms a (3 × 3) ordered overlayer [9]. The segregation exhibits a significant face-specificity. The segregation on the (755) face is many times larger than that on the Rh(331) face [6]. The segregation of boron in our sample started from 700 K. If we assume that the segregation processs is in equilibrium in the range 700–1000 K, the segregation energy is −71.5 kJ/mol.

The observed shape of the segregation curve and the negative segregation energy are in contrast with the features of other common impurities, such as Si in Pt(111) [14] and C in W(100) [15] and Fe(100) [16], where the equilibrium concentration of segregated Si and C increased with decreasing temperature. Negative segregation energies have been measured for some alloy systems, e.g. Cu–Pd, Cu–Sn [17] and Ni–Ru [18]. We may assume that in such systems, including ours, the segregation is essentially controlled by diffusion of the segregation component from the bulk to the surface. It should be pointed out that the surface concentration of boron segregated at a given temperature (700–1000 K) reached the final value almost immediately (1–2 s) and did not change during cooling.

From the XPS data, we have calculated 5.8×10^{14} surface boron atoms/cm² at the highest boron coverage. On the Rh(111) surface, the upper limit of the surface boron would be about a quarter of a monolayer (4×10^{14} boron atoms/cm²) if it were all at the surface [4].

An analysis of the width of the He I UPS upon the segregation of boron did not reveal any changes in the work function, indicating that the dipole

moment produced by surface boron is very small. This is consistent with the similar Pauling electronegativities of B (2.0) and Rh (2.2), which suggests that charge transfer between these elements is minimal.

Independently of the coverage, the B(1s) level appeared at 187.8 eV in the XPS. The peak broadened slightly with increase of the surface boron concentration. The peak exhibited 3.5 eV FWHM at saturation. This value is significantly larger than that observed for B(1s) on the Mo(100) surface after the adsorption of diborane [19,20]. We assume that the B(1s) peak is composed of two or more overlapping peaks. The unusually large value for the FWHM can be explained by the different states of the boron. This assumption involves random filling of the surface by isolated boron monomers and dimers, or the formation of islands.

The segregation of boron on Rh foil produced a photoemission peak at 8.6 eV. The intensity of the peak increased and it shifted slightly to higher binding energy with increase of the surface concentration of boron (difference spectra in fig. 2B). In a UPS study on iron borides, peak due to emission from the boron 2p, 2sp^2 and 2s states were identified [12]. The bonding picture proposed there was one of 2sp^2 hybridization, which increases with the B/Fe ratio due to increasing B–B bonding. The B(2sp^2) level is located at 7.0 eV for Fe$_2$B and at 10.0 eV for FeB. According to the study by Joyner and Willis [12], the 2sp^2 emission is due to a B–B interaction. As the intensity of the photoemission peak at 8.6–9.0 eV increased with the boron level on Rh, we may assume (in harmony with the XPS results) that a B–B interaction also exists in our system. A similar conclusion was reached by Stair et al. [19,20] for the B/Mo(100) system.

The B(2p) level would be expected at around 4.0–5.0 eV. The detection of this level is doubtful in our case (fig. 2B). One possible reason is that the cross-section is very low.

Overall, the XPS and UPS results suggest that the segregated boron on Rh foil mainly forms dimers or islands instead of isolated monomers.

4.2. The nature of the B + O layer on Rh foil

The energy location and peak shape in the XPS, UPS, AES and ELS (in the electronic range) can be utilized to infer certain properties of the B + O overlayer. The drastic changes in the boron features due to oxygen adsorption suggest a direct interaction between boron and oxygen.

The formation of a B–O species on the Rh(111) single-crystal surface and the preferential oxidation of impurity boron on Rh were first demonstrated by Semancik et al. [8] using high-resolution electron energy loss spectroscopy (HREELS). While oxygen adsorption on the clean Rh(111) surface at 320 K produced a single strong feature at 530 cm^{-1}, in the presence of boron impurity, new vibrational losses developed at 730 and 1450 cm^{-1}. When the

crystal was heated briefly to 960 K, the peak at 530 cm^{-1} subsided, but the other HREELS features became more intense, with an upward shift to 735 and 1590 cm^{-1} In contrast with the behavior of chemisorbed oxygen on clean Rh(111) (which begins to desorb at 850 K) the B–O species at the surface was found to be stable on heating to above 1100 K in vacuum.

The adsorption of oxygen on a "boron-free" surface ($R_B = 0.003$) produced the O(1s) level at 530.2 eV (fig. 7A). On a boron-containing Rh surface, the dominant O(1s) peak at 300 K appeared at 531.8 eV with a shoulder at 530.2 eV. At the highest boron concentration, an additional shoulder developed at 532.6 eV, suggesting the formation of another kind of species on the surface. The B(1s) level also moved to higher energy, from 187.8 to 191.5 eV (fig. 7B). These large shifts in both the O(1s) and B(1s) levels unambiguously demonstrate a strong chemical interaction between B and O. The shoulder for O(1s) at 530.2 eV indicates that a small proportion of the adsorbed oxygen is bonded to Rh atoms.

The appearance of an intense loss at 9.4 eV in the EELS when boron-containing Rh foil was exposed to a small amount of oxygen also supports our conclusion. As this loss was not observed following the adsorption of oxygen on a clean surface, it can safely be attributed to the formation of a B–O species. The 9.4 eV loss was detected at a temperature as low as 159 K, this observation, together with the time-dependence of the development of the 9.4 eV loss feature at 170–250 K indicates that the reaction between B and O proceeds slowly but surely even at low temperatures.
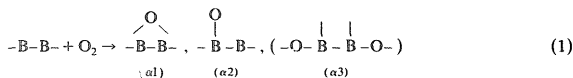
The formation of a B–O bond is also justified by the fine structure of B and O(KVV) AES signals at 300 K. The Auger transition of adsorbed oxygen on a boron-containing surface appeared at 513 eV at low oxygen exposure. With increase of the oxygen coverage, the intensity of this peak increased and a transition at 518 eV for adsorbed oxygen on Rh sites also developed (fig. 4).

A similar drastic change was found in the B(KVV) transition (fig. 3). The observed line shape is very similar to that observed after oxidation of polycrystalline boron at 300 K when the surface contains domains of elemental and oxidized boron [21]. In spite of the fact that Auger spectroscopy is not an exact tool for the determination of the stoichiometry of surface compounds, the similarities of the Auger line shapes for bulk B_2O_3 [22], H_3BO_3 [22], chemisorbed oxygen on boron [23] and in our system strongly suggest that the segregated boron on Rh foil is also oxidized.

In order to learn more about the nature of the B–O species formed, we analysed the spectral changes occurring at higher temperatures. When the temperature was increased from 300 to 400 K, the O(1s) level at 531.8 eV in the XPS broadened on the higher-energy side, and at above 400 K the O(1s) level appeared at 532.6 eV (fig. 8A). This spectral change in the O(1s) level indicates a transformation of the B–O bond. This change was not accompanied by a detectable alteration in the B(1s) level, the first sign of the

broadening of the B peak was observed only above 580 K. This change in the B(1s) level suggests that the boron became more positive in character and the B–O species was very probably transformed into B_2O_3. *This conclusion is supported by the fact that the core level spectra observed above 720 K for O(1s) and B(1s) agree well with that of B_2O_3 [22].*

If the above consideration is taken into account, we can count with the occurrence of the following surface reactions between oxygen and the boron-contaminated surface. It appears that the oxygen interacts first with the boron and then with the free Rh atoms:

$$
-B-B- + O_2 \rightarrow \overset{\displaystyle O}{-B-B-}, \quad -\overset{\displaystyle O}{\underset{\displaystyle |}{B}}-B-, \quad (-O-\overset{\displaystyle |}{B}-\overset{\displaystyle |}{B}-O-) \tag{1}
$$
$$
\quad\quad (\alpha 1) \quad\quad (\alpha 2) \quad\quad\quad (\alpha 3)
$$

New spectroscopic features

AES (eV)	XPS (eV)	UPS (eV)	ELS (eV)
513	191.5	5.9	9.4
158	532.6		
171			
185			

$$
2\,Rh + O_2 \rightarrow \overset{\displaystyle O \quad O}{\underset{\displaystyle (\beta)}{Rh-Rh}} \tag{2}
$$

New spectroscopic features

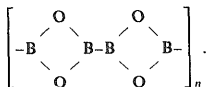| UPS (eV)	XPS (eV)	AES (eV)
5.5	530.2	518.0

Species α are formed slowly even at 159 K at low exposures, as demonstrated by ELS measurements (figs. 5 and 6), while species β is obtained only at higher exposures when all the surface boron has interacted with oxygen. In addition to these surface species, we may also expect the transitory formation of species

$$
Rh \overset{\displaystyle O}{\diagup} {}^{\diagdown} B
$$

We   presume that species $\alpha 3$ best characterizes the structure formed. The m   important compounds of this type of B–O bond are the boron

suboxides [24], which contain groups in the form of $\alpha3$ and may form a linear chain:

$$\begin{bmatrix} & O & & O & \\ & \diagup \diagdown & & \diagup \diagdown & \\ -B & & B-B & & B- \\ & \diagdown \diagup & & \diagdown \diagup & \\ & O & & O & \end{bmatrix}_n .$$

When the temperature is increased to above 400–500 K, the cleavage of the B–B bond starts, as indicated by the shifts in the B(1s) level (fig. 8B) and the O(2p) emission (fig. 9) to higher binding energies. This process is completed at about 750 K, when the $2sp^2$ hybrid state at 8.6–9 eV in the UPS, due to the B–B bond, is no further detectable, and when a polymer-like B_2O_3 species is produced

$$\begin{bmatrix} & | & \\ & O & \\ & | & \\ & B & \\ & \diagup \diagdown & \\ O & & O \\ \diagup & & \diagdown \end{bmatrix}$$
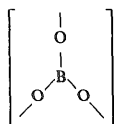
New spectroscopic features

UPS (eV)	XPS (eV)
6.4	532.6
	192.4

Further processes are indicated by the decrease in the O Auger signal above 900 K and by the reappearance of the elemental boron feature (187.8 eV) in XPS. As we do not expect the decomposition of the stable B_2O_3 species (the dissociation energy of B–O is 787 kJ/mol), we assume a further segregation of boron and a reaction between B_2O_3 and elemental boron

$$B(s) + B_2O_3(s) \rightleftharpoons B_2O_2(g) + BO(g),$$

the heat of reaction is 141.1 kJ/mol [25]. The occurrence of this reaction in the present case is supported by the observation that upon heating the Rh foil containing the B–O complex to high temperature we detected desorbing species at 54 and 27 amu (B_2O_2 and BO, respectively): the peak temperature was 1050 K. Note that partial oxidation of bulk boron leads to the formation of $(BO)_x$ which vaporizes at 1300 K, as B_2O_2, and disproportionates on condensation [25].

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