



# Article XPS Studies of the Initial Oxidation of Polycrystalline Rh Surface

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**Abstract:** Increased interest in the oxidation process of polycrystalline rhodium, observed in recent years, is the result of its application in exhaust catalytic converters. However, most studies have involved sample surfaces with low Miller indices. In our research, we investigated polycrystalline rhodium foil containing crystallographically different, highly stepped, µm-sized crystallites. These crystallites were exposed to identical oxidizing conditions. To determine crystallographic orientation, the electron backscattering diffraction (EBSD) method was used. To investigate the initial stages of oxidation on the individual crystallites of Rh, X-ray photoelectron spectroscopy (XPS) studies were performed. The results obtained for the individual crystallites were compared and analyzed using chemical state quantification of XPS data and multivariate statistical analysis (MVA).

Keywords: polycrystalline rhodium; spatially resolved XPS; multivariate analysis

# 1. Introduction

In the last twenty years, there has been a rapid development of both the science of catalysis and its applications in industry. This has become possible mainly due to the progress of science in the synthesis of new materials, although the use of new methods in conducting catalytic processes has also had a very positive impact on the development in this field of knowledge [1]. The widespread introduction of surface physics analytical methods to identify and determine the structure of catalyst active centers and the mechanism of their interaction with catalytic reaction reagents has also greatly contributed to the development of catalysis and its applications [2]. The so-called "surface science" approach to explaining the course and speed of catalytic reactions has significantly influenced the advances in heterogeneous catalysis [3].

In this fundamental approach to the development of heterogeneous catalysis, it was first proposed to study the structure–activity relationship using surface sensitive methods and techniques. According to this approach, the analysis of a specific catalytic process should begin with the study of well-ordered single crystals under ultra-high vacuum conditions. Next, it is necessary to proceed to the study of processes occurring at increased pressure in the gas phase (in order to solve the so-called problem of "pressure gap") as well as to more complex catalytic systems from crystalline samples with a more developed area to clusters and polycrystalline samples (to solve the so-called "material gap" problem). The case studies cited in [1–3] prove the effectiveness of the proposed approach in studying the reactivity of the active ingredient particles for the subsequent molecular design of catalysts with improved performance (activity, selectivity, and stability) and show that the development of surface science in application with heterogeneous catalysis is in line with current trends.

Rhodium is a transition metal from the IX group and crystallizes in a face-centered cubic (fcc) structure. A pure Rh crystal exhibits surfaces of distinct steric orientations labeled by Miller indices. The Rh {111} are the most dense within hexagonal atom configuration and Rh {110} surfaces have the

most open surfaces with a rectangular surface unit cell. The real crystal surface may be misoriented with one of the low index planes by some tilt.

Transition metal surfaces are usually not finished in such an ideal form as the arrangement of atoms in the crystal volume. Due to the high density of hanging bonds, free surface energy can be minimized by rearranging atoms that form new bonds or by transferring charge between hanging bonds using a mechanism called auto-compensation. Rearrangement of atoms can cause a lattice stress that increases surface free energy. The combination of these two opposite effects must lead to the creation of a reconstructed surface to minimize free surface energy. The instability of ideal surfaces becomes evident when chemical molecules adsorb onto the surface.

Careful and thorough analysis of the oxidation processes of elements from the platinum group has allowed us to state that for each of the metals, there is a critical temperature or range of temperatures above which the oxide film, instead of continuing to thicken, completely disappears. If the metal is then quenched rapidly, it is seen to be bright and oxide-free [4].

Chemisorption studies of oxygen on the Rh (111) and Rh (100) planes indicated that adsorbed oxygen formed a (2 × 2) structure at about  $\Theta$  = 0.25 ML coverage on both (111) and (100) rhodium surfaces [5]. Increased molecular oxygen exposure reversibly formed a c (2 × 2) phase on the Rh (100) surface. The desorption of oxygen from the Rh (111) surface begins at 670 K. With oxygen coverage of approximately  $\Theta$  = 0.5 ML, the adsorbate structure on the Rh (111) surface is formed [6]. Further oxygen dosing consumes the existing phases and forms a (8 × 8) structure or (1 × 1) if atomic oxygen is used [7–9].

Platinum group metals deposited as the finest particles on the surface of oxides are widely used as catalysts for various redox processes. Thin oxide layers formed on the surface of transition metal catalysts are well known as one of the factors controlling the increase or inhibition of the catalytic activity of metal catalysts [10–13]. In studies conducted for Rh single crystals, it was found that the reaction with oxygen was not very sensitive to the surface structure and that the formation of oxides led to a lower reaction speed [14,15]. The authors of these works found that well-ordered, ultra-thin oxide layers were formed on the Rh surface. In addition, by using high-resolution XPS, Scanning tunneling microscopy (STM), Surface X-ray Diffraction (SXRD), and Density functional theory (DFT) calculations, it has been shown that at moderate oxygen pressures, self-limited growth of the three-layer O–Rh–O film on Rh (111) is observed. In later studies of the CO oxidation process carried out by SXRD methods and mass spectroscopy [5], it was observed that this ternary oxide structure is much more active than the metallic Rh at a temperature as low as about 500 K, while bulk Rh oxide was not active at all.

Recently, several industrial corporations have been conducting intensive scientific research and implementation studies on the development of catalyst technology based on polycrystalline materials. For this reason, we decided to undertake research related to the catalytic properties of polycrystalline rhodium films. Our goal was to determine the behavior of individual high-index rhodium crystallites during oxygen adsorption.

A polycrystalline Rh sample can serve as a kind of "surface structure library" [13]. In the field of view of the microscope (e.g., secondary electron microscope or low energy electron microscope), a set of randomly spaced surface orientations can be probed. This allows for differences in the oxidation-sensitive behavior of the Rh sample to be observed in one experiment. In this paper, in order to examine the initial stages of oxidation on individual Rh crystallites, spatially separated XPS studies were performed [16]. The results obtained for individual crystallites were presented, compared, and analyzed. The quantitative chemical state analysis of XPS data is assisted by complementary information from multivariate statistical techniques such as principal component analysis (PCA). The theory of the PCA method is shortly reviewed with special emphasis on the issues related to XPS spectra analysis. The use of PCA in this study aims to show differences between crystallites directly using a 2-dimensional model of the XPS spectra.

#### 2. Results and Discussion

In the introduction to the work, we noticed that the formation of the ternary O–Rh–O layer was observed in the early stages of the rhodium oxidation process [5]. This process was already noticed at room temperature, although the three-layer formation was only fine-tuned at 520 K [17]. The authors of the last publication also stated that pre-oxidation carried out with molecular  $O_2$  caused a heterogeneous increase in oxide as opposed to the atomic oxygen experiments. They also concluded that structural defects were more effective places for  $O_2$  dissociation and stabilizing the RhO<sub>2</sub> stoichiometry oxide.

Based on the results of the above work, we selected a range of polycrystalline rhodium oxidation temperatures at 423–668 K. The kinetics of the Rh oxidation process was studied by registration of spatially-resolved XPS spectra at various stages of oxidation and at different temperatures. By repeating experiments at different temperatures and calculating the total oxide rate, an Arrhenius plot for the oxidation process could be constructed. This served to determine the activation energy for four analyzed areas marked from (1) to (4). As expected from the above results, differences in activation energies were found for the investigated Rh surfaces.

#### 2.1. X-ray Photoelectron Spectroscopy (XPS) Results

In order to compare the initial oxidation stages for different crystallographic grains of polycrystalline rhodium foil, spectra from four relatively large crystallites were registered. After cleaning the sample, according to the procedure described in the experimental section, we recorded the spectra of the Rh 3d level. They consisted of a single doublet characteristic for metallic rhodium, producing sharp peaks at binding energies of 307.53 and 312.25 eV, which represent the Rh  $3d_{5/2}$  and Rh  $3d_{3/2}$  levels, respectively. During oxidation, as expected, a slight broadening of the spectra is observed due to the formation of the oxide and the appearance of its signal shifted toward higher binding energies. Figure 1 presents a comparison of the Rh 3d level spectra for areas (1) and (4) before and after 75 min of oxidation. At first glance, they look very similar. After decomposition, however, one can notice slight differences in oxide concentration for different areas of interest. O1s oxygen level at about 530 eV was also observed, as shown in the insets in Figure 1. The data from the oxygen region had, however, a poor signal to noise ratio. There are several reasons for this low intensity. First, the data were collected from only 4% of channels of the detector in order to provide that the data were collected only from a small area of the sample (i.e., the mm-size area of interest). The disadvantage of this approach is, of course, the low intensity of the spectra. Oxygen spectra also have a much smaller, compared to rhodium, relative sensitivity factor (RSF) in XPS, which is another reason for a weak O1s level signal. The low intensity of this level and its location near the Rh  $3p_{1/2}$  peak did not allow for reliable standard quantitative analysis.

The rate of oxidation, labelled as R, was estimated based on the contribution of oxide part within the Rh 3d level for each region of interest. The formation of oxide resulted in a chemical shift in XPS spectrum. Peaks from oxidized rhodium shifted about 0.8 eV toward higher binding energies with respect to the metallic peaks. Deconvolution allowed us to estimate the amount of oxide by comparing the intensities of metallic and oxide components in the Rh 3d spectrum. The increase of oxide contribution was observed both as a function of oxidation time and as an increase in temperature.

Calculation of the oxide formation rate for different temperatures allowed us to construct the Arrhenius plots. These were used to estimate the activation energies for the initial stages of the oxidation process for different crystallites. The plots are presented in Figure 2. Linear fitting to Arrhenius plots allowed us to suppose that lower activation energies were relevant to crystallites (2) and (4), which in both cases was about 0.15 eV. However, the areas marked as (1) and (3) corresponded to the slightly higher values of activation energy of 0.24 and 0.21 eV, respectively.



**Figure 1.** Rh 3d spectra: (**a**) from area (1) before oxidation; (**b**) from area (1) after 75 min of oxidation at 668 K; (**c**) from area (4) before oxidation; (**d**) from area (4) after oxidation at the same conditions as in (**b**); Oxygen signal is presented in the insets.



Figure 2. Arrhenius plots based on the data from four analyzed crystallites.

Activation energy is one of the basic parameters that determine the rate of chemical reaction involving a catalyst. The resulting activation barriers for the catalyzed reaction are smaller than for the non-catalyzed reaction, and therefore the overall reaction rate is higher.

Similarly, in our study, the measured activation energy values were very low. In addition, it can be seen that the crystallite structure affects the activation energy value. Lower  $E_a$  values were observed for crystallites (2) and (4) compared to crystallites (1) and (3), which means that higher surface corrugation promotes the oxidation process.

# 2.2. Diagnostics of Data Collected from Various Rh Crystallites by Principal Component Analysis

In this study, the dataset generated by the XPS technique contained 160 photoelectron spectra measured at different times of exposure to oxygen and under different thermal conditions, and is therefore ideally suited for data analysis using PCA. After developing the PCA model, a practical plot

was generated. Figure 3 presents a one-dimensional PCA score plot for a set of XPS spectra; the score values for PC1 are along the y-axis, while the x-axis simply denotes a spectrum number. The set of spectra was arranged with respect to the number of crystallites: (1) the first 40 spectra; (2) the samples from 41 to 80; (3) the samples from 81 to 120; and (4) the last 40 samples. It is advisable to name the spectra in a way that reflects the experimental conditions (i.e., temperature and time of exposure to molecular oxide). In this case, the object name 'T668min75' indicates that this spectrum is measured by oxygen exposure at 668 K for 75 min.



**Figure 3.** Plot of scores in the PC1 direction as calculated for four polycrystalline rhodium crystallites. The spectra out of the 95% confidence limit were selected.

The most important data changes were actually described by the first principal component; PC1 explains 99.93% of the total variance in the XPS spectra. Thus, the PC1 model fits the original data with a high confidence level. The plot showed a similar trend for each crystallite. At the bottom of the figure, there are scores calculated for a clean Rh metallic surface. For each crystallite, five spectra for clean Rh were recorded, which corresponded with five different temperatures. As can be seen, the one-dimensional PCA model does not create separate group of spectra for each crystallite, however, the trends on the graph suggest that various experimental conditions such as temperature and the oxidation exposure time influenced the spectra. Therefore, checking the appearance of particular spectra on the score plot gives valuable chemical information for later use in the analysis. There are two groups of spectra that are extremes (lie outside the 95% confidence level limit - dashed upper line) that come from the crystallographic orientation of (2): (-24 2 -29) and (4): (-4 14 1), determined by EBSD. From the plot, it can be read that they corresponded to the highest temperature (668 K) and long exposure times (60–90 min), except for one spectrum. This means that these spectra have influence on the model in this direction (PC1) and, as they lie on the opposite side of the scores for clean Rh, the conclusion is that these extremes display the least proportion of the metallic Rh component (i.e., the crystallites (2) and (4) are most susceptible to oxidation process). Thus, the one-dimensional PCA model concentrates on describing the variation due to oxide exposure and it can be used for quantitative information acquisition. For this purpose, the score vector for PC1 was normalized with respect to the score for the Rh metallic spectrum and named as reduced scores.

Another conclusion can be obtained from Figure 4. The plot shows reduced score values on PC1 at various temperatures for 75 min of the oxygen exposure time. It can be concluded that at low temperatures below 578 K, there is only a small amount of oxide on the Rh metallic surface, which varied from 1% to 3% as the reduced scores indicate. At high temperatures above 578 K, the reduced scores of each crystallite clearly increased, revealing that the formation of the Rh oxide on the Rh

surface was faster. Under these conditions, two crystallites, (2) and (4), showed the greatest change in oxide concentration. The PCA model, although generally not suitable for directly determining chemical component concentration, has revealed in such study the potential to obtain quantitative information about Rh oxide coverage during the exposure to oxygen. The PCA conclusions support the reliability of the traditional analysis based on peak-fitting procedures.



**Figure 4.** Plot of reduced scores in the PC1 direction as calculated for four polycrystalline rhodium crystallites under different temperatures at 75 min of the oxidation exposure.

## 3. Materials and Methods

#### 3.1. Polycrystalline Rhodium Sample

As a sample, a  $10 \times 12 \text{ mm}^2$  rectangular piece of polycrystalline rhodium film with a purity of 99.99% (MaTecK, Juelich, Germany) and with a thickness of 0.2 mm was used. The sample was mounted on a sample holder transferred to a ultra-high vacuum (UHV) station equipped with a spatially-resolved VG-Scienta, Uppsala, Sweden R3000 hemispherical analyzer. Cleaning was carried out by argon sputtering, annealing, and chemical treatment with oxygen. Ion cleaning was carried out at 300 K using argon ions (10  $\mu$ A, 3 keV). The sample was then annealed for 30 min to 1123 K. To remove carbonaceous impurities, additional chemical treatment was carried out using oxygen at 773 K until the XPS spectra did not contain a carbon signal.

Polycrystalline rhodium foil, consisting of many crystallites of different sizes with different structures, is an example of a set of randomly distributed crystallites with different crystallographic orientations and provides promising insight into structure dependence and the heterogeneity of catalytic reactions. Figure 5 shows images of the polycrystalline surface of the rhodium sample obtained from an optical confocal microscope. The clean surface presented in Figure 5a had many scratches and imperfections, but clear grain boundaries could also be observed. The fact that they are indeed crystallites of different orientations becomes apparent after the high oxidation process. Such an attempt was made for the same sample in a separate experiment, using a flow-through high pressure reactor. The sample was exposed to 1.5 bar of oxygen at 873 K for 30 min. As a result, the crystallites were colored with at least six different shades, as shown in Figure 5b. Most grains were rather small, but one could also find some crystallites of about 1 mm in size. In our study, four such larger grains were selected to minimize the risk of skipping (e.g., due to the slack on the sample manipulator mechanism). Four chosen areas are marked in Figure 5 and differ in hue after high oxidation, which may indicate that they had different reactivity. To set the sample during XPS measurements, two tantalum and two silver markers were spot-welded in the corners of the sample.

By scanning the sample along X and Y axes, the coordinates of the center point of each marker were found and were then used to scale the area analyzed by XPS.



**Figure 5.** Confocal microscopy image of the polycrystalline surface of the rhodium sample: (**a**) after cleaning, with four marked regions of interest; (**b**) after "high oxidation" in flow-through reactor.

# 3.2. Crystallographic Orientation of Rh Foil Domains

Identification of the rhodium foil crystallography was obtained by EBSD. It is a scanning electron microscope-based microstructural-crystallographic characterization technique commonly used in the study of crystalline or polycrystalline materials [18]. The technique provides information about the structure, crystal orientation, and phase of the material. A flat surface was prepared by polishing and rinsing with acetone. EBSD measurements were carried out using the Field Electron and Ion Co. Hillsboro OR, USA (FEI) Quanta 3D Field Emission Gun (FEG) and scanning electron microscope (SEM), equipped with an EDAX Inc. Mahwah NJ, USA Genesis Orientation Imaging Microscopy (OIM) back-scattered electron diffraction recording and analysis kit.

An EBSD analysis was carried out from the supplied rhodium sample in the area of about  $7 \times 9 \text{ mm}^2$ . The SEM (scanning electron microscopy) micrograph recorded using a back-scattered electron detector from these conditions is shown in Figure 6. Crystal orientation maps are often displayed in the so-called inverse pole figure (IPF) coloring [18]. Figure 6a shows the inverse pole figure map (IPF) of the rhodium sample. Figure 6b shows all Euler RGB maps, where the face-centered cubic (fcc) matrix grains have been marked in red, while a continuous network of green dots decorating the grain boundaries has been indexed as a body-centered cubic (bcc) phase. The fcc and bcc phases exhibit an orientation relationship that can be established from the EBSD results. The pole figures corresponding to the phases are shown in Figure 6c.



**Figure 6.** Scanning electron microscopy (SEM) orientation image microscopy: (**a**) Inverse pole figure (IPF) map showing the grain orientation on the rhodium sample; (**b**) pole figure; (**c**) inverse pole figure color coded map.

## 3.3. Spatially-Resolved X-ray Photoelectron Spectroscopy (XPS) Analysis

In order to perform the XPS experiment, the sample was introduced into the UHV system consisting of preparation and analysis chambers. The cleaning, annealing, and oxidation were done in a preparation chamber (base pressure  $\leq 5 \times 10^{-10}$  mbar). Photoemission studies were performed in an analysis chamber at the base pressure  $\leq 2 \times 10^{-10}$  mbar. Non-monochromatized Al K $\alpha$  radiation (1486.6 eV) was used as an excitation source. The main axis of the source was oriented at 55° with respect to the norm of the sample surface. The photoemission spectra were obtained) at the normal angle with respect to the surface. In order to calculate the rate of oxidation, experimental data were fitted to asymmetric line-shapes by using CasaXPS<sup>®</sup> software (Casa Software Ltd., Teignmouth, UK) after modeling standard Shirley background.

In spatially-resolved XPS studies, we took advantage of the imaging properties of the energy analyzer [16]. Photoelectrons emitted from the surface due to the X-ray irradiation are focused and the linear image is created in the non-dispersive plane of the analyzer, while at the same time the XPS spectrum corresponding to each point in the line is established in the dispersive plane. Data acquisition takes place by using a two-dimensional detector (micro-channel plate). XPS data were collected from multiple channels of the detector for the chosen regions of the Rh sample. The advantage of such a spatially separated method in oxidation studies is that all test areas are exposed to exactly the same oxygen pressure and temperature for the same time in one experiment.

Applying spatially resolved XPS to individual stepped Rh (hkl) domains of a polycrystalline Rh foil used as a set of randomly distributed crystallites with different crystallographic orientations, we demonstrated the dependence of the Rh oxidation rate on the surface structure. Measurements performed at an oxygen partial pressure in the  $10^{-5}$  mbar range and at temperatures from 423 K to 668 K enable determining the activation of the initial oxidation of Rh.

The sample was oxidized in an  $O_2$  atmosphere (1·× 10<sup>-5</sup> mbar) for 7, 15, 30, 45, 60, 75, and 90 min. The temperatures of oxidation were 423, 493, 578, 623, and 668 K. After sample oxidation, we began analyzing the sample composition using spatially-resolved XPS. For the analysis, we selected four different high-index crystallites, whose positions on the sample are shown in Figures 5 and 6. The crystallographic orientations of these four crystallites found in EBSD are as follows: (-17 -8 11), (-24 2 -29), (9 5 -6) and (-4 14 1). Orientations of particular crystallites with respect to unit cell as well as their structure models are shown in Figure 7.



**Figure 7.** Structure models of the four chosen and analyzed areas of the sample, denoted as (1), (2), (3) and (4); Miller indices found by electron backscattering diffraction (EBSD) are presented in the insets.

## 3.4. Statistical Multivariate Analysis to Examine XPS Data for Chosen Rh Crystallites

In the process of matching the curve to the registered spectrum, and thus obtaining information on the proportion of occurrence of each chemical state, there is always some uncertainty. The uncertainty of the XPS curve fitting results is due to the choice of background subtraction method, statistical fluctuations of the registered intensity, etc. Therefore, to make quantitative analysis more reliable, multivariate statistical insight can be used to examine XPS data. The main advantage of the multivariate statistical analysis (MVA) applications to spectral analyses such as XPS is that it includes a complete set of data at once, and no mathematical function describing the shape of the line is required. This approach allows, therefore, to create a global model, in particular, it is a very effective way to compare spectra obtained in different experimental conditions and at different spatial coordinates on the surface, which simplifies time-consuming analysis of large datasets.

Principal component analysis (PCA), one of the most popular method for multivariate analysis, is fundamentally different from standard curve-fitting methods. It gives the possibility of obtaining a quick differentiation of the share of chemical components in the set of obtained photoelectron spectra by applying the geometric interpretation of the spectrum as a vector in n-dimensional space. The number n denotes the number of measurement points (e.g., binding energy values) for which XPS spectra were recorded, usually a large number like 200 or more. PCA assumes that any set of spectra described by a linear combination of two or more pure chemical components can be decomposed into orthogonal abstract components: the principal components. The principal components create a new, low-dimensional space. A detailed description of PCA can be found elsewhere (see e.g., [19,20]). Typically, when PCA is applied to spectral data with different composition, or from different stages of the chemical/physical process being investigated, the goal is to reduce dimensions by using space with one or two principal components (PCs). Thus, the n-dimensional problem goes from n to the 1D or 2D-principal component model. The PCs model "well distributes" the most diverse spectra in the PC1–PC2 space, which can be displayed graphically.

Thanks to the use of PCA, the dataset is reduced to two cross-product matrices. These matrices, commonly called scores and loadings, can be used to visualize the quantitative relationship between spectra and the relationships between the original variables (characteristic binding energies of spectral peaks), respectively. More specifically, each spectrum has its own score value (contribution) in PC1, PC2, and so on. A small score value means that the spectrum is the most typical (like average spectrum), whereas the high score value means that it is extreme.

The most common is the graphical visualization of the score vector for PC1 versus the score vector for PC2. These are the two directions along which the data swarm exhibits the largest and the second largest "spread". However, in some cases, the use of 1-dimensional score vector (i.e., plotting the score vector for PC1 versus the spectrum number) could give valuable information in a simple way. For spectroscopic data, one can see the quite high % variance captured by PC1 (i.e., 99.8%), which means that the set of spectra is composed of a very strong systematic component. If it is a case, the score value could have a semi-quantitative chemical interpretation (i.e., contains chemical composition information about the Rh3d doublet in this case).

In spectroscopic application, there are several options to normalize the data to compensate for individual spectral differences due to experimental errors. In this study, before using PCA, each raw spectrum was normalized to the sum of the intensities. Then, PCA was performed using PLS Toolbox v.8.8.1 (Eigenvector Research, Manson, WA, USA) for MATLAB (MathWorks, Inc., Natic, WA, USA).

## 4. Conclusions

In the research carried out for the purposes of this publication, we dealt with the initial stage of the oxidation process of a polycrystalline rhodium sample containing differently oriented crystallites. Individual Rh crystallites were subjected to identical oxidation conditions. Using EBSD, a full crystallographic characterization of individual domains was performed, providing a kind of a set of randomly distributed crystallites with different crystallographic orientations. Spatially resolved XPS measurements allowed us to determine the oxidation state of Rh on four randomly selected Rh crystallites. On the basis of spatially-resolved XPS studies, we determined the oxidation rates of the four selected crystallites and determined the activation energy of the oxidation process. We used the PCA method to study the differences between the results obtained for analyzed crystallites. Based on the results obtained, we can conclude that a polycrystalline Rh foil consisting of differently oriented µm-sized crystallites provides a suitable model for studying orientation-dependent surface processes. Moreover, the initial stages of Rh oxidation in the  $10^{-6}$ - $10^{-5}$  mbar oxygen pressure range revealed an orientation-dependent oxidation process: higher surface corrugation promotes the oxidation process. A detailed study of the role of the steps and kinks in the surface oxidation of Rh requires testing for further crystallites with a different orientation compared to the four crystallites examined in this paper. We intend to conduct such research in the near future.

**Author Contributions:** M.T.: XPS measurements and data analysis, writing. G.B.-C.: PCA and MVA analysis, writing. A.B.: Investigation, EBSD analysis, supervision, writing. All authors discussed the results and commented on the manuscript. All authors have read and agreed to the published version of the manuscript.

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