Structural and Chemical State Changes in Rh on Al$_2$O$_3$/NiAl(100) Studied by NEXAFS, XPS and AFM†

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We have studied the structural and chemical changes of Rh on Al$_2$O$_3$/NiAl(100) depending upon heat treatment, and the oxidation reaction of atomic sulfur on Rh/Al$_2$O$_3$/NiAl(100) surface under atmospheric environment by means of Near Edge X-ray Absorption Fine Structure, X-ray Photoelectron Spectroscopy and Atomic Force Microscopy techniques. Rh nanoclusters are formed on the Al$_2$O$_3$/NiAl(100) surface after the deposition of Rh. With elevated temperature, the aggregation of Rh atoms occurs on the Al$_2$O$_3$ layer at 600 K. At the temperature range from 600 to 1000 K, Rh atoms diffuse and dissolve into the NiAl(100) substrate through Al$_2$O$_3$ layer. On the other hand, the S 2$p$ XPS and S K-edge NEXAFS studies indicates the noticeable oxidation of the atomic sulfur adsorbed on Rh/Al$_2$O$_3$/NiAl(100) under atmospheric environment. In this oxidation reaction, not only the reaction temperature but also the degree of O$_2$ partial pressure seems to be important.

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I. INTRODUCTION

Al$_2$O$_3$ is often used as a support material for nanoparticles in several catalysts. In the field of automotive catalyst, the nano-particles of platinum group metals are supported on Al$_2$O$_3$. These catalysts play an important role in the reduction of NO$_x$ and the oxidation of CO. Such catalysts are named three way catalysts. Those performances are frequently degraded by some deactivation factors because of the use in the severe environment. The high temperature causes a diffuse of catalyst metals and it leads to an aggregation of metals or dissolution into support materials. Besides, the residual sulfur in fuel induces the poisoning of the catalyst surface [1].

Metal dissolution into Al$_2$O$_3$ occurs under high temperature environment about 1000 K. It is supposed that metal atoms can diffuse into Al$_2$O$_3$ support through the defects of Al$_2$O$_3$. In this case, the dissolved metal cannot contribute to the catalytic reaction. Actually, it was reported that a part of Rh atoms was dissolved into Al$_2$O$_3$ support material by oxidation at 873 K [2]. We have also revealed the dissolution of Rh into the Al$_2$O$_3$/NiAl(100) substrate at 1000 K by X-ray Photoelectron Spectroscopy (XPS) [3]. However, the changes of XPS spectra related with the morphological changes of the catalyst surface are not studied well.

The sulfuric atmosphere as low as a few ppm causes the sulfur adsorption on the catalyst surface. The adsorbed sulfur disturbs the other purification reactions, so-called Sulfur-Poisoning [4, 5]. The dissociation of a sulfur-containing molecule is the main problem, because the formed atomic sulfur covers the catalyst surface [6, 7]. On the other hand, the reaction between atomic sulfur and oxygen leads to a removal reaction of sulfur from the catalyst surface, which can be available to the easy recycle of the catalyst metals [4, 8]. The excellent performance of Rh for the sulfur removal reaction was reported by some studies [4, 5]. Therefore, the oxidation of atomic sulfur on Rh surface is of great interest in the field of an automotive catalyst.

The aim of this work is firstly to investigate the structural and chemical changes of Rh on Al$_2$O$_3$/NiAl(100) depending upon heat treatment, and secondarily to reveal the oxidation reaction of atomic sulfur on Rh/Al$_2$O$_3$/NiAl(100) surface under atmospheric environment by means of Near Edge X-ray Absorption Fine Structure (NEXAFS), XPS and Atomic Force Microscopy (AFM) techniques.

II. EXPERIMENTAL

A commercially available NiAl(100) single crystal (10 mm$^6$ diameter, 2 mm thickness, Surface Preparation Laboratory Inc.) was mechanically polished with 0.05 µm Al$_2$O$_3$ to a mirror finish. The NiAl(100) crystal was cleaned by the alternating cycles of Ar$^+$ ion sputtering (3 keV, 2 µA, 30 min) to remove sulfur, carbon and oxygen contaminations and annealing at 1100 K for 30 min by an electron bombardment in an ultrahigh vacuum (UHV) chamber. The base pressure was better than $4 \times 10^{-8}$ Pa. The cleanliness of NiAl(100) surface was verified by XPS measurements (S 2p, C 1s and O 1s).

A well-ordered ultrathin α-Al$_2$O$_3$ layer was grown on exposing the cleaned NiAl(100) to O$_2$ (~1000 L) at 500 K and subsequently annealing at 1000 K for 5 min [9]. 1.0 ML of rhodium was deposited on the Al$_2$O$_3$ thin layer at room temperature with Rh vapor from

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an ultra-pure Rh wire (purity: 99.9%) set in an electron beam evaporator. After deposition, the sample was heated at 600 K or 1000 K for 5 min. Four types of samples were prepared in this work, which were Al$_2$O$_3$/NiAl(100), Rh/Al$_2$O$_3$/NiAl(100) as Rh deposited, Rh/Al$_2$O$_3$/NiAl(100) heated at 600 K or 1000 K. The Rh/Al$_2$O$_3$/NiAl(100) surface covered with atomic sulfur was prepared in the UHV chamber. The atomic sulfur was obtained by the adsorption of (CH$_3$)$_2$S : DMS at 90 K, and subsequently the thermal dissociation with annealing up to 300 K. The sulfur oxidation reaction was promoted under O$_2$ environment ($2.7 \times 10^{-5}$ Pa for 1h) at 523 K or in air (for 3 days, at 300 K).

XPS spectra at Rh 3$d$ and S 2$p$ regions were measured for the prepared samples. The XPS measurements were recorded by use of the concentric hemispherical electron energy analyzer (PHOIBOS 100-5ch, SPECS) with MgK$_{α}$ X-ray (1253.6 eV). All binding energies were referenced to Ni 3$p_{3/2}$ peak position of NiAl alloy at 853.0 eV [10]. The thickness of Al$_2$O$_3$ layer was 4-5 Å estimated from the Al 2$p$ XPS spectrum [11]. The coverages (ML) of Rh and sulfur were obtained with their XPS peak intensities in Rh 3$d$ and S 2$p$ regions (1ML corresponds to the area density of fcc Rh(100) surface atoms, $1.37 \times 10^{13}$ atoms/mm$^2$).

After the sample was taken out from the UHV chamber, the surface morphology was observed with NanoScope III-a (Veeco Instruments) with tapping mode AFM. Rh L$_{3}$-edge and S K-edge NEXAFS measurements were carried out under atmospheric condition (ex-situ NEXAFS) at the soft X-ray double crystal monochromator beamline BL-3 on Hiroshima Synchrotron Radiation Center (HSRC). In order to investigate the oxidation of atomic sulfur under atmospheric environment, the ex-situ XPS data was obtained for the sample exposed to air once.

### III. RESULTS AND DISCUSSION

#### A. Surface morphology

Figures 1(a)-(d) show the AFM images obtained from Al$_2$O$_3$/NiAl(100), Rh/Al$_2$O$_3$/NiAl(100) as-deposited and Rh/Al$_2$O$_3$/NiAl(100) heated at 600 K or 1000 K. A lot of stripe structures are observed on the Al$_2$O$_3$/NiAl(100) surface in Figure 1(a), consistent with the other reports [9, 12, 13]. These structures are thought to grow preferentially along the crystal directions. The stripes disappear when the surface covered with Rh layer.
FIG. 2: Rh 3d XPS spectra for the Rh/Al₂O₃/NiAl(100) systems after different thermal treatments. The main peak positions are matched each other, and the area colored with green signifies the difference between each spectrum and that of bulk Rh.

FIG. 3: Rh L₃-edge NEXAFS spectra for the bulk Rh and the Rh/Al₂O₃/NiAl(100) systems after heat-treatment at 600 K or 1000 K.

B. Chemical change in Rh/Al₂O₃/NiAl(100)

Figure 2 shows the Rh 3d XPS spectra for the Rh/Al₂O₃/NiAl(100) systems after different thermal treatments. In order to compare these peak shapes, the main peak positions are matched each other. The area colored with green signifies the difference between each spectrum and that of bulk Rh. One can find that the peak width of as-deposited surface becomes broader than that of bulk Rh. According to our previous study [3], the first layer Rh which directly bonds to the Al₂O₃ layer has the peak at higher binding energy side than bulk Rh, because such Rh atoms are picked some electrons up to the Al₂O₃ layer. On the other hand, the Rh atoms in second layer or more show the corresponding peak position to the metallic Rh such as bulk Rh [14]. Therefore, Rh atoms seem to form clusters with at least two layers on Al₂O₃/NiAl(100) surface. The peak width becomes narrower when the sample is heated at 600 K. Then the spectral shape is considerably corresponding to that of bulk Rh. This change indicates the aggregation of Rh atoms on the Al₂O₃ layer. In contrast to the former two spectra, the spectrum of the Rh/Al₂O₃/NiAl(100) heated at 1000 K can be seen with a sharper and symmetric peak shape. Furthermore, the peak position (307.50 eV) undergoes a higher shift in comparison with bulk Rh (307.20 eV), and the satellite structure locating at higher binding energy side disappears. Similar change in a XPS spectral shape was observed on nickel aluminides [10]. They have reported that the positive shifts of Ni 2p₃/2 energy level increases, the satellite structure disappears, and further, the peak shape of Ni 2p₃/2 becomes symmetric with
the decrease of nickel concentration in the alloys. Such changes can be well understood with the charge-transfer satellite. Therefore, the Rh atoms are likely to form the alloy like state at 1000 K. Then, we can confirm that the Rh atoms dissolve into the NiAl(100) substrate through the Al₂O₃ layer, occurred by the heat-treatment at 1000 K.

Rh L₃-edge NEXAFS are shown in Figure 3. These spectra are normalized by the edge-jump each other, and then, we can discuss the chemical state per one Rh atom. The spectral shape, such as the peak height and the width, is quite similar between the bulk Rh and the Rh/Al₂O₃/NiAl(100) heat-treated at 600 K. Thus, one can also verify the aggregation of Rh atoms at 600 K by Rh L₃-edge NEXAFS analysis. The positive shift of the main peak position from that of the bulk Rh indicates that these Rh clusters interact with the Al₂O₃ layer and some contaminations, because the sample is exposed to the atmosphere at once. When the sample is heated at 1000 K, the peak intensity of the main peak at 3007.0 eV decrease, and another structure appears at the higher energy side. We can speculate that the new structure shows the bonds between Rh-Al or Rh-Ni. These Rh atoms are assumed to exist as single atom and/or small cluster, because the spectrum has two peaks assigned to alloy and metallic states. A model for the Rh state on Al₂O₃/NiAl(100) with elevated temperatures is shown in Figure 4.

C. Oxidation of sulfur on Rh/Al₂O₃/NiAl(100)

Figure 5 shows the S 2p XPS spectra for atomic sulfur on Rh/Al₂O₃/NiAl(100) as-deposited surface, which were measured after O₂ treatment at 523 K and after exposing to air (ex-situ).

Figure 6 shows the S K-edge NEXAFS spectra for atomic sulfur on Rh/Al₂O₃/NiAl(100) under atmospheric environment, S/Rh(100), and K₂SO₄.

FIG. 4: A model for the Rh chemical states on Al₂O₃/NiAl(100) with elevated temperatures.
162 eV (vertical line), which is assigned to atomic sulfur. In previous study [3], we have revealed the desorption of atomic sulfur from the Rh/Al2O3/NiAl(100) surface caused by oxidation (2.7 \times 10^{-5} \text{ Pa of O}_2 \text{ at } 523 \text{ K}). However, the amount of sulfur desorption was quite a little, and most of the atomic sulfur remains on the surface without being oxidized in that study. Therefore, a similar feature to S/Rh(100) was obtained for the sulfur on Rh/Al2O3/NiAl(100) after O2 treatment, shown as the spectrum at the center of Figure 5. After the exposure to air, the intensity of the main peak at 162 eV decreases and a broad peak appears from 165 eV to 171 eV. These chemical states are assigned to SOx species (x = 1-4) [4]. The S K-edge NEXAFS spectrum for this sample, shown in Figure 6, also has both peaks for the atomic sulfur at 2470.7 eV and the oxidized sulfur state at 2479.1 eV. N. Pangher et al. have reported that the SO on Cu(100) shows a peak at about 2475 eV [15]. And K2SO4 shows the peak at 2481.70 eV. Thus, the chemical state of the oxidized sulfur atom on the Rh/Al2O3/NiAl(100) can be assigned to SO2 or SO3, because the peak lies at the middle position between SO and SO4 states. Noticeable oxidation of the atomic sulfur occurs under atmospheric environment even at 300 K. From these results, it is found that not only the reaction temperature but also the partial pressure of O2 significantly affects the oxidation reaction of the atomic sulfur on the Rh/Al2O3/NiAl(100) surface. This oxidation reaction is important in the removal reaction of sulfur from catalyst surfaces, because it is known that such sulfur contaminations desorb from catalyst surfaces as SO2. Consequently, one can expect the healing effect from the sulfur poisoning by using that oxidation reaction occurring under atmospheric environment.

IV. CONCLUSION

We have investigated the structural and chemical changes of Rh on Al2O3/NiAl(100) depending upon heat treatment, and the oxidation of atomic sulfur on Rh/Al2O3/NiAl(100) surface under atmospheric environment. The deposited Rh forms nanocluster with 1-3 Rh layers formed on the Al2O3/NiAl(100). The Rh 3d XPS and Rh L3-edge NEXAFS results indicates the aggregation of Rh atoms on Al2O3 layer at 600 K, and the diffusion and the dissolution of Rh atoms into the NiAl(100) substrate through Al2O3 layer at the temperature range form 600 to 1000 K. The S 2p XPS and S K-edge NEXAFS studies shows that the atomic sulfur adsorbed on Rh/Al2O3/NiAl(100) surface undergoes the noticeable oxidation under atmospheric environment. Therefore, it is supposed that the degree of O2 partial pressure significantly affects the oxidation reaction of the atomic sulfur on the Rh/Al2O3/NiAl(100) surface.

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