論　文

ZrNi 上の Pd 被覆膜の真空加熱による状態変化

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Changes in the Chemical and Crystallographic States of Pd-overlayers on ZrNi Plate with Vacuum Heating

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Abstract

Pd coatings on Zr-based alloys are effective in protecting the alloy surface from poisoning impurity gases. To evaluate the stability of this layer regarding heat cycles, changes in the Pd overlayer on ZrNi plates with vacuum heating were studied as a model system with X-ray photoelectron spectroscopy (XPS) and X-ray diffractometry (XRD). XPS measurements revealed that the Pd coating caused a significant reduction in contaminant oxygen and carbon from the surface. XRD measurements of the Pd overlayer suggested that the internal stress of the Pd layers was annealed out and Ni atoms were dissolved in the layer below 800℃. At higher temperatures, PdZr was formed with the surface having a change in its nature.

1. INTRODUCTION

Hydrogen-gettering metals and alloys have wide applicability to fuel processing for thermonuclear fusion reactors[1−5]. Among them, attention has been paid to Zr-based alloys because of their excellent properties such as sufficiently low equilibrium pressure suitable for storage[6−8], high equilibrium pressure at relatively low temperature for

supply[9,11], high absorption rate for recovery[11-15], and so on[17-21].

Activated alloy surfaces are, however, easily deactivated by reactions with impurity gases such as H_2O, CO, CO_2 and hydrocarbons to form obstruction surface layers[22-26]. One solution to avoid the deactivation of these alloys is to coat the alloy surfaces by protective layers[27,28]. For this purpose, the present authors have studied the applicability of Pd coating which is expected to act as protective layer for impurity gases and permeation window of hydrogen isotopes. Accordingly, the functional alloys coated with Pd are expected to have a longer life time than the bare alloys in practical use. Furthermore, the getter unit could be downsized because of the reduction of poisoning effects. Despite the evidence of effectiveness of Pd coating against impurity gas exposures[28], details of the change in Pd overlayer with heatings are not fully understood yet.

Since heating and cooling operations will be cyclically repeated in their applications, the Pd overlayer is anticipated to alter its properties due to mutual diffusion of Pd and constituents of substrate. Therefore, effects of heatings on Pd overlayer should be studied in detail from both physicochemical and crystallographic points of view.

The present paper describes changes observed with X-ray photoelectron spectroscopy (XPS) and X-ray diffractometry (XRD) in the Pd overlayer with vacuum heating.

2. EXPERIMENTAL

2.1. Sample preparation

A ZrNi alloy ingot was purchased from Japan Metals & Chemicals Co. It was prepared with argon arc melting of the stoichiometric mixture of Zr and Ni powders. It was sliced into plates of $10 \times 10 \times 0.5$ mm in size with a wire saw. The surface of ZrNi plate was ground by a polishing machine with waterproof abrasive paper (#2000) for 2 hrs to remove the surface oxide layer. Subsequently, it was rinsed in an ethanol and acetone bath using ultrasonic cleaning method. After the sample being dried in air, the ZrNi plate was coated with palladium by use of a conventional sputtering apparatus, ULVAC SBR-1104, operated with argon plasma at 200 W at room temperature. The overlayers were 20 and 100 nm in thickness, which were prepared for XPS and XRD measurements, respectively. The sputtering system was pumped by an oil-diffusion pump backed with an oil-sealed rotary pump. The base pressure of the system was 4×10^{-4} Pa. The pressure of argon gas and acceleration voltages for argon ions were 0.5 Pa and 3 kV, respectively. Hereafter, the coated ZrNi will be denoted as Pd/ZrNi.

2. 2. XPS and XRD measurements

The apparatus used was an ultra high vacuum (UHV) system equipped with XPS. The system was evacuated with a sputter ion pump and a turbomolecular pump backed with an oil-sealed rotary pump. The base pressure of the system was routinely below 7×10^{-7} Pa. The Pd／ZrNi sample was mounted on a Ta-heater plate attached to the sample holder made of stainless steel. It could be heated up to 1000℃. The temperature of the sample was monitored with a Pt／Pt-Rh(13%) thermocouple spot-welded to the back side of the heater. Changes in the surface chemical state of the Pd／ZrNi sample with vacuum heating were analyzed through XPS measurements. The MgKα radiation (1253.6 eV) with 400 W power was used as probe for XPS. The energy of photoelectrons was measured by use of a double pass cylindrical mirror analyzer (PHI 12-255) and calibrated by referring the Au4f$_{7/2}$ peak as 83.7 eV[29].

XRD method was used to examine crystallographic changes in the surface layer of the Pd／ZrNi. The sample was heated at a given temperature for 10 min in a quartz tube attached to a vacuum system designed for annealing and thermal desorption analysis. The sample could be heated up to 900℃. After being cooled down to room temperature, the sample was took out in room air for XRD measurements. XRD patterns were recorded by a X-ray diffractometer, Phillips PW1700. The probe was the CuKα line operated at 0.1572 nm with 1200 W power. The incident angle of X-rays was fixed at 3° to the surface plane to observe thin subsurface layer.

3. RESULTS

3. 1. XPS measurement

Figure1 shows the change in the wide range XPS spectra of Pd ／ZrNi with temperature. The as-prepared surface was covered with Pd with a small amount of carbon impurity. The intensity of Pd3d peak was drastically decrease by heating above 600℃, whereas the C1s peak became predominant and Zr3d peak appeared above 700℃. It is apparent that both the peak intensity and binding energy of
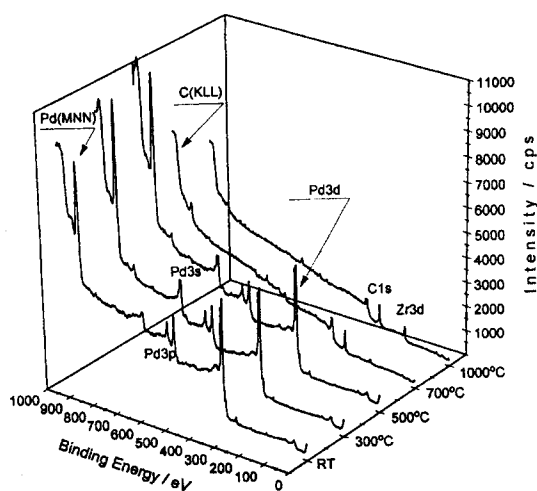

Fig. 1 Changes in wide range XPS spectra of Pd／ZrNi with vacuum heating.

observed peaks in these spectra changed with heating temperature. It is noteworthy that no Ni2p peaks were observed throughout the XPS measurements.

Changes in the surface atomic compositions of observed elements are plotted against temperature in Fig.2. In a low temperature region below 400℃, the atomic fraction of Pd increased with increasing temperature and rapidly decreased with temperature between 400 and 700℃ to reach a level below 10 at.%. It further decreased gradually to 5 at.% at 1000℃. The atomic fraction of carbon showed the reverse movement to that of Pd: namely, it increased to 90 at.% between 400 and 600℃ and kept its value upto 1000℃. On the other hand, Zr appeared at 700℃ and its intensity gradually increased to 10 at.% with heating temperature to 1000℃. The ratio of Pd and Zr was roughly 1 : 1 around 900℃.

Figure 3 shows changes in the binding energies of $Pd3d_{5/2}$, C1s and $Zr3d_{5/2}$ photoelectron peaks with temperature. This figure shows that the $Pd3d_{5/2}$ peak kept its position at 334.9 eV to 500℃. Then it gradually shifted toward the higher binding energy side to reach a constant value of 336.1 eV around 900℃. Namely, the chemical state of palladium changed above 500℃. In the high temperature region above 700℃, the $Zr3d_{5/2}$ peak appeared at 179.5 eV. This value was higher than that of metallic Zr. It indicates that zirconium compounds were formed on the surface. On the other hand, the C1s peak kept its position at 284.4 eV to 500℃, and shifted toward the lower binding energy side to reach a constant value of 284.2 eV. It indicates that the chemical state of carbon atoms was changed by formation of new compounds above 500℃.
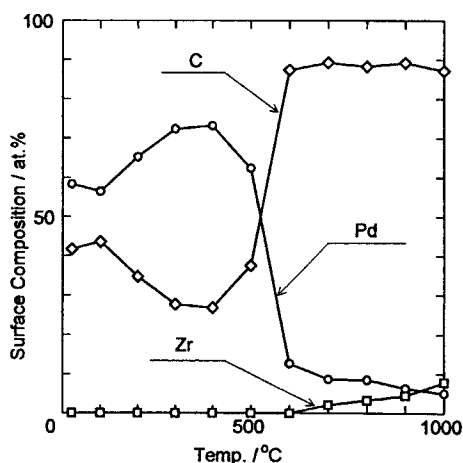

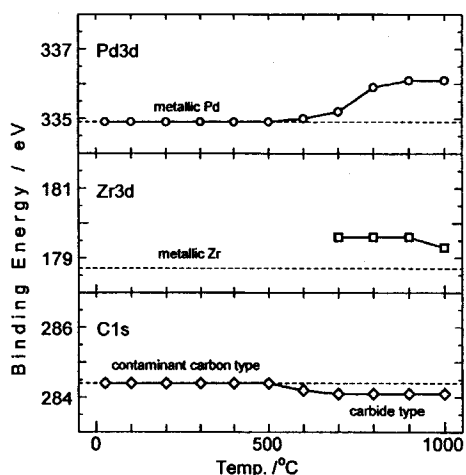Fig. 2 Changes in the surface atomic fractions of Pd/ZrNi with vacuum heating.

Fig. 3 Changes in the binding energies of $Pd3d_{5/2}$, $Zr3d_{5/2}$ and C1s with vacuum heating.

3. 2. XRD measurement

Figure 4 shows the XRD patterns for the polished ZrNi (bottom) and Pd／ZrNi samples after vacuum heating for 10 min at given temperatures. The angles of diffraction observed for the bare ZrNi plate were in good agreement with that of JCPDS data[30]. No diffraction peaks except Pd was found for the as-prepared Pd／ZrNi, indicating that whole surface area was covered with Pd. The observed peaks were attributed to metallic Pd. They shifted toward the higher angle side with increasing heating temperature to 600℃. However, diffraction patterns drastically changed above 700℃ : namely, new diffraction peaks appeared which could be assigned to PdZr[30].

Figure 5 shows the shifts of diffraction peaks of Pd(111), (200) and (220) with heating. The angles of diffraction from nominal Pd are indicated in the figure with dashed lines : namely, planes of Pd(111), (200) and (220) have to be observed at $2\theta = 40.12$, 46.66 and 68.09° , respectively. It is apparent from this figure that diffraction peaks of the as-prepared sample appeared at lower angles in comparison with those for the nominal peaks. These
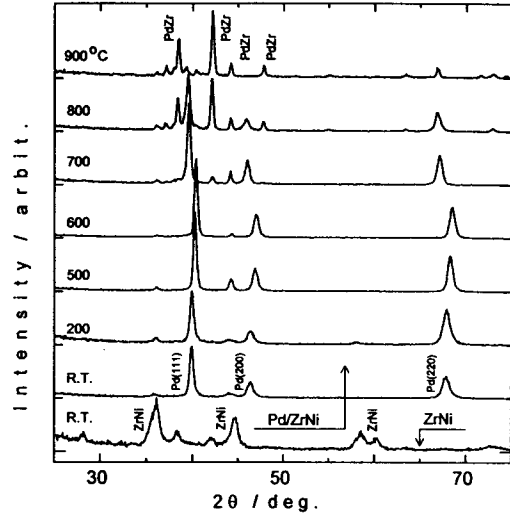

Fig. 4 XRD patterns for the mechanically polished ZrNi plate (bottom) and Pd／ZrNi after vacuum heating for 10min at respective temperatures.
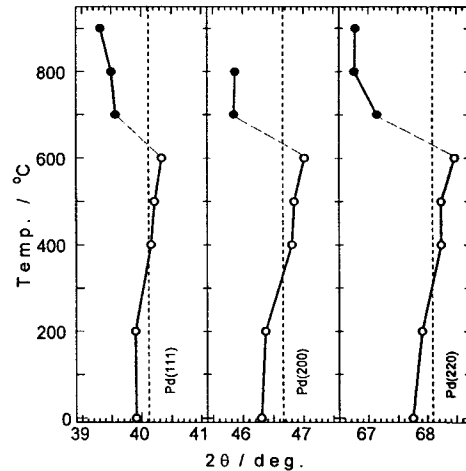
Fig. 5 Shifts of the diffraction peaks of Pd(111), (200) and (220) with vacuum heating.

peaks continuously shifted toward the higher angle side with increasing temperature to 600℃. Then, they discontinuously jumped to the lower angles and showed a slight decreasing tendency above 700℃.

Figure 6 shows changes in the lattice parameter of Pd with temperature. The lattice parameter was evaluated from the Pd(220) peak which was not overlapped with other peaks. The calculation was carried out by assuming that the structure of Pd overlayer kept face centered cubic under the whole experimental heating temperature. This figure shows that the lattice parameter of Pd for the as-prepared sample, 0.391 nm, was lager than the nominal value of Pd, 0.389 nm. The lattice parameter continuously

Fig. 6 Changes in the lattice parameters of Pd overlayer with vacuum heating.

decreased to reach about 0.387 nm with increasing temperature to 600℃, and then discontinuously jumped to reach constant value of 0.396 nm above 800℃.
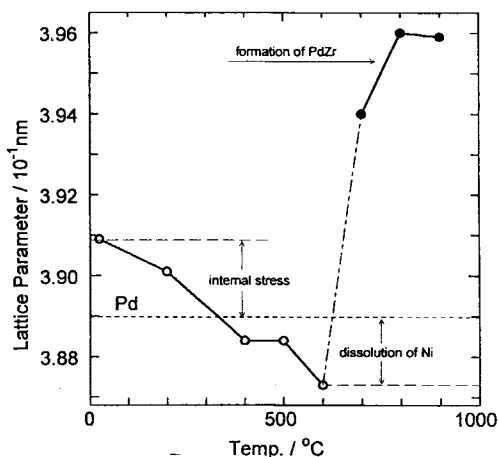
4. DISCUSSION

In the low temperature region from 28 to 400℃, the lattice parameter of Pd decreased to below the nominal value of Pd, 0.389 nm. It has been observed by Kinbara et al. that the diffraction peaks of evaporated thin gold film shift to larger angles of diffraction than the nominal values of Au because of the internal stress accumulated in the film, and the observed deviations disappear after annealing at 230℃[31]. This fact suggests that the initial decrease in the lattice parameter toward 0.389 nm is due to the annealing of the internal stress in the Pd overlayer. On the other hand, there was no noticeable changes in chemical states of Pd and C in the temperature range below 400℃.

The further decrease in the lattice parameter should caused by other mechanisms. In this temperature range, XPS measurements revealed that $Pd3d_{2/5}$ peak shifted toward the higher binding energy side. It indicates that the chemical environment of Pd changed with heating. The change most plausibly results from the progress of mutual diffusion among Pd, Zr and Ni. This is supported by the appearance of Zr on the sample surface at high temperatures as shown in Figs.1 and 2. Since Ni and Pd atoms dissolve each other in the whole concentration ratio to produce a solid solution, the change in the lattice parameter could be explained by Vegard's rule as[32],

$$\alpha_{\text{solid solution}} = N_{Pd} \, \alpha_{Pd} + N_{Ni} \, \alpha_{Ni} \qquad\qquad (1)$$
$$(\alpha_{Pd} = 0.389 \text{ nm}, \ \alpha_{Ni} = 0.352 \text{ nm})$$

where α and N represent the lattice parameter and atomic fraction, respectively. Eq. (1) indicates that the lattice parameter decreased with increasing Ni concentration. Therefore, the decrease in the lattice parameter in the temperature range from 400 to 600℃ is attributed to the dissolution of Ni atoms in Pd overlayer. From Eq.(1), the atomic fractions of Pd and Ni were calculated as 95 and 5 at.% at 600℃, respectively. The small surface atomic fraction and the low atomic sensitivity of Ni are very likely to responsible for the lack of Ni peaks in the XPS spectra.

The shift of C1s above 600℃ is ascribed to the formation of Zr-carbide because C1s shifts toward the lower binding energy on forming metal carbide[29]. This is consistent with the chemical shift of $Zr3d_{5/2}$ toward the higher binding energy side. Therefore, it is concluded that the most of carbon and a part of zirconium atoms form Zr-carbide. Since Pd does not form carbide under the present experimental conditions, the shift of $Pd3d_{5/2}$ peak should be ascribed to formation of PdZr and/or dissolution of Ni atoms.

The new diffraction peaks appeared in XRD patterns at high temperatures above 700℃ as shown in Fig.4. According to the JCPDS data[30], they could be assigned to an intermetallic compounds of PdZr in which Ni atoms appear to be dissolved in a little extent. These XRD observations are in good agreement with XPS: namely, the surface atomic ratio of Pd and Zr was almost unity in high temperature region above 700℃ (Fig.2), suggesting the formation of PdZr.

On the other hand, it has been confirmed by XPS measurements that metallic Zr is an essential substance for Zr-alloys to be active to hydrogen absorption[18]. Therefore, it is indispensable to keep surface metallic Zr clean in order to maintain their gettering capabilities in absorbing hydrogen isotopes. As a result of the Pd coating on ZrNi plate, no oxygen and other molecules containing oxygen were observed on the as-prepared Pd/ZrNi surface (Fig.1), suggesting that Pd coating is promising to improve surface properties of Zr-based alloys. According to our previous study, a Pd-coated Zr-alloy (Pd/Zr$_3$Al$_2$) showed durability against exposure to N_2 and CO_2[28]. Although, the exposure caused the reduction of absorption rate of deuterium, the extent of the reduction for Pd/Zr$_3$Al$_2$ was smaller than that of bare Zr$_3$Al$_2$. In addition, Pd/Zr$_3$Al$_2$ showed little differences in the kinetic parameters from those of bare Zr$_3$Al$_2$ for ab/desorption of hydrogen isotopes as well. Namely, this kind of Pd-overlayer acts

as protective surface barrier against impurity gases and also as hydrogen permeation channel.

The increase in the surface atomic fraction of C above 600℃ is ascribed to the diffusion and surface segregation of carbon atoms in Pd overlayer. The driving force should be the low solubility of C in Pd. Carbon might be included in the Pd layer from impurity gases such as hydrocarbons during sputter coating because of the poor vacuum conditions of the present apparatus (4×10^{-4}Pa or higher). It is well known that water molecules react with carbon atoms at relatively low temperatures to form H_2, CO and CO_2[33] as follows,

$$H_2O \longrightarrow H_2(g) + O(a) \qquad (2)$$
$$C + O(a) \longrightarrow CO(g) + CO_2(g) \qquad (3)$$

where C and O(a) indicate carbonaceous deposits and adsorbed oxygen atoms on the sample surface, respectively. Previous thermal desorption spectroscopic measurements showed that surface carbon and/or adsorbates containing carbon on Pd-coated Zr-alloy could be removed by the reaction with H_2O to form CO and CO_2[28]. Although occurrence of such reaction processes largely depends on surface metal elements and its states, XPS measurements revealed that Pd-carbide was not formed in this study. Therefore, presence of carbon on the surface has little significance because it could be removed by reactions with oxidative reactants.

With respect to the practical use of Pd coating onto Zr-based alloys, it is possible to maintain original nature of Pd overlayer by limiting the operation temperature below 500℃ in order to avoid formation of alter layer caused by the mutual diffusion of Pd and constituent elements of a substrate. Data for ab/desorption kinetics of hydrogen isotopes in/from PdZr are highly required from the viewpoint of high temperature operation.

CONCLUSIONS

The present study is summarized as follows.
1. Pd coating reduced and/or removed contaminant oxygen and species containing oxygen from the Zr-based alloy surface.
2. Carbon atoms included in the Pd overlayer produced surface carbonaceous deposits by diffusion and surface segregation at high temperatures above 500℃. Presence of carbon on the surface has little significance because it can to be removed as CO and CO_2 through the catalytic reactions with oxidative reactant such as H_2O.

3. The operation temperatures of the Zr-based alloys with Pd overlayer should be limited below 500°C to avoid degeneration caused by the mutual diffusion of Pd and substrate.

4. Formation of an intermetallic compound, PdZr, took place above 700°C.

5. There is no noticeable change in chemical states for Pd overlayer below 500°C. Concerning to the change in crystallographic structure, on the other hand, the reduction of internal stress and the dissolution of Ni in Pd overlayer took place being observed as the decrease in lattice parameter of Pd.

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