High Responsiveness Induced by Palladium Deposition on Thin Film Actuator of LaNi$_{5}$ Hydrogen Storage Alloy$^{*1}$

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The unimorph actuator of the LaNi$_5$ thin film deposited on polyimide substrates can be expected as a sensor and/or a controller of hydrogen gas flux in various hydrogen-related devices, since controlling the hydrogen concentration in the film by pressure change drives this actuator reversibility. In this study, the effect of the palladium deposition was investigated on the mechanical response of this thin film actuator. It was shown that the initiating time (incubation period) for the actuation to be measured after hydrogen gas exposure was reduced from 100 to 1 s by the palladium deposition. This significantly improvement of the mechanical response was attributed to the change in the rate determining steps: the dissociation of hydrogen gas molecules on the sample surface for the sample without palladium deposition, and hydrogen diffusion in 1 s by the palladium deposition. This high-permeability of hydrogen in palladium film at room temperature resulted in the high responsiveness.

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1. Introduction

Hydrogen storage alloys have been used to directly react and store a volume of hydrogen gas as much as 1000 times larger than that of the alloys.$^{11}$ The LaNi$_5$ hydrogen storage alloy is a potentially attractive material with which to develop high power bimetal actuators because of its ability to expand up to 25% in volume by hydrogen absorption.$^{22}$ This high-volume expansion of the LaNi$_5$ hydrogen storage alloy generates a tremendous force, indicated by the plastic deformation of a thick-walled 18-8 stainless steel reaction cell.$^{33}$ If a new actuator using a hydrogen storage alloy can be developed, this power can be triggered by a change in the absolute hydrogen pressure around the sample. Thus, a unimorph structural actuator has been constructed, driven by the volume expansion of a hydrogen storage LaNi$_5$ alloy film.$^{44}$ A hydrogen storage La-Ni alloy film, prepared by flash evaporation has shown a reversible shape change on hydrogen absorption and desorption.$^{45}$ In previous works, the LaNi$_5$ alloy has been pulverized after a number of hydrogen adsorption and desorption cycles.$^{5,6}$ A thin film of the alloy has shown a high resistance to pulverization,$^{7,8}$ thus, the thinning enhances the material’s fatigue resistance. The pressure-composition isotherm usually exhibits a plateau region as mixture of hydride and metal phases, whereas almost linear isotherm can be obtained for the LaNi$_5$ alloy films deposited with more disordered crystal structure.$^{99}$ In such case we expect a long lifetime for a new actuator driven by a LaNi$_5$ alloy thin film. In order to apply this material to a practical actuator in the field of hydrogen energy systems, the composition dependence$^{1010}$ and load dependence$^{55}$ of the strain produced by a shape change have been studied for the LaNi$_5$ alloy film. However, the low actuator responsiveness is a serious problem for applications directed to a broad market. To enhance this responsiveness, the dissociation rate of hydrogen gas has been accelerated by a platinum catalyst.$^{11,11}$ Furthermore, palladium often also acts as a catalyst. Thus, in the present work, using magnetron sputtering vapor deposition we have coated the surface of a polyimide-supported LaNi$_5$ film with palladium in order to investigate its effects on the shape change responsiveness of this new unimorph structural actuator.

2. Experimental Procedure

LaNi$_5$ hydrogen storage alloys were prepared by arc melting (ACM-DS01 DIAVAC Ltd.) and subsequent annealing for homogenization. The block sample was pulverized by several hydrogen cycles of adsorption and desorption using ultra high purity H$_2$ gas (7N); the resulting powder was sieved to obtain a mean grain size of 35 μm (3.5 ± 1.0 × 10$^{-5}$ m) in diameter. To obtain hydrogen storage thin films that showed a high resistance to pulverization and fatigue, thin films were prepared by flash evaporation using the pulverized LaNi$_{5}$ powders onto a polyimide substrate (Kapton (R) 500V, DU PONT-TORAY Co. Ltd.).$^{10,12}$ The tungsten heater and substrate temperature were 2273 and 414 ± 19 K, respectively. The deposition time was 392 ± 4 s. The base pressure was less than 1.0 × 10$^{-3}$ Pa, and the deposition rate was 0.7 nm/s (0.7 × 10$^{-9}$ m/s). The dimensions of the polyimide substrate were 18 × 10$^{-3}$ m in width, 18 × 10$^{-3}$ m in length, and 125 μm (1.25 × 10$^{-4}$ m) in thickness (SEM observation; JSM 6300F, JEOL). The chemical composition of the deposited hydrogen storage alloy film was analyzed by energy dispersive X-ray spectroscopy (EDS: JSM-6301F, JEOL Ltd.) as LaNi$_{5.0.0.1}$. The crystal structure was confirmed by X-ray diffraction (TF XRD; X’ Part MRD, Philips). X-ray diffraction revealed that the deposited LaNi$_5$ film has an amorphous structure.

To enhance the responsiveness of the LaNi$_{5.0.0.1}$ unimorph actuator film, a palladium deposition was performed by ion-
sputtering (E1010, Hitachi Science Systems Ltd). A palladium thin film of 75 nm ($7.5 \times 10^{-8}$ m) in thickness, as evaluated by SEM observation (JSM 6300F, JEOL) was obtained, when the sputtering potential, current, power, pre-sputtering time and sputtering time were RF500V, 0.4 A, 200 W, 60 s and 30 s, respectively. The prepared films were activated using ultra high purity H$_2$ (7 N) at 60 bar in a reaction tube made of 18-8 stainless steel. An activation was performed by hydrogen absorption for 600 s and evacuation for 600 s. The temperature during the activation process was 300 K. The adsorption/desorption cycle was repeated 30 times. To desorb any remaining hydrogen, the change in material shape was monitored for 600 s. The activated unimorph actuator was then transported to a reaction bed made of silica glass. After an evacuation to a hydrogen gas pressure of 0.12 to 0.3 MPa, the adsorption/desorption cycle was repeated 30 times. 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untreated sample, but 1 s for the palladium deposited sample. We confirmed that the palladium deposition shortened the incubation period.

4. Discussion

4.1 Dominant factors in hydrogen gas absorption

In order to confirm the effects of the palladium deposition on the responsiveness of the actuator, the rate-determining step (the slowest kinetic step) in the reaction mechanism was ascertained. Based on the kinetic model of hydrogen solution, suggested by Fromm,\(^{13}\) the initial hydrogen absorption rate \((V)\) was expressed by the following equation taking into account the hydrogen gas pressure \((P)\) and the Boltzmann factors.

\[
V = \frac{dN_{H_2}}{dt} = k \times P^n \times \exp(-A/RT)
\]

Here, \(N_{H_2}, R, k, n, A\) and \(T\) are the solved hydrogen atomic fraction, gas constant, rate constant, reaction order, apparent activation energy and absolute temperature, respectively. Because the solubility limit of hydrogen atom in LaNi\(5\) is small, the atomic fraction almost corresponds to the fraction of hydride phase, which results in a large volume change. If the strain rate of shape change, \((d\Delta e'/dt)\), is equal to the hydrogen absorbed rate \((dN_{H_2}/dt)\), the value of \(d\Delta e'/dt\) at a constant temperature, could be expressed by the following equation.

\[
\frac{d\Delta e'}{dt} \propto \frac{dN_{H_2}}{dt} \propto P^n
\]

Based on eq. \((4)\), the \(n\) value, an indicator of the dominant reaction stage, was determined. Figure 3 shows the relationship between the applied hydrogen pressure, \(P_{H_2}\), and the rate of strain generated by the shape change, \(d\Delta e'/dt\), of the hydrogen storage LaNi\(5\) alloy film with and without palladium deposition.

The \(n\) value was equal to one for the untreated LaNi\(5\) thin film. Since \(n = 1.01\) for untreated sample, the hydrogen gas molecule decomposition at the interface was a dominant factor.\(^{14}\) A lanthanum oxide thin film, probably formed on the LaNi\(5\) thin film surface from residual oxygen gas during vapor deposition, decreased the hydrogen transmission speed. Thus, the oxide film should probably be an obstacle to control the dissociation of hydrogen gas molecules on the sample surface.

The rate of the film’s shape change at 0.3 MPa of hydrogen gas pressure was higher than those at low pressures of hydrogen gas, as shown in Fig. 3. If the high hydrogen gas pressure increases the molecular dissociation of the hydrogen gas at the interface, the high rate of shape change, induced by a high pressure of 0.3 MPa, might be explained as rate determining step of decomposition. From the theoretical consideration, the pressure dependence value; \(n\) must be one or smaller than one. That is, the higher rate at 0.3 MPa shown in Fig. 3 is the result of different reaction mechanisms, such as some partial reduction of surface oxides was occurred or new surface was generated by small crack spreading, where the reaction probability of hydrogen on the new surface was much smaller than that on Pt deposited surface.

4.2 Effects of palladium deposition

On the other hand, this significantly modified mechanical response by the palladium deposition might be attributed to a switching of the reaction rate determining steps. When \(n = 0.5\), the dominant factor should be the activation energy of atom diffusion.\(^{13}\) The \(n\) value was equal to 0.64 for the palladium deposited LaNi\(5\) thin film, as shown in Fig. 3. The palladium deposition, which formed a palladium thin film of 75 nm \((7.5 \times 10^{-8} \text{ m})\) thick, enhanced the decomposition rate of hydrogen gas molecules at the interface. The palladium deposition should bring about a change to a permeation/diffusion of the hydrogen atoms into the film. The rate determining reaction after the palladium deposition was no
longer the dissociation of hydrogen gas molecules on the sample surface, but the hydrogen diffusion in the film.

In addition, pinholes usually exist in a palladium thin film of this thickness. The palladium film could not perfectly cover the 1.1 nm (1.1 × 10⁻⁶ m) thick LaNi₅ film. Therefore, the dissociated hydrogen atoms can easily diffuse on the film surface and migrate into the film. If the palladium deposition tremendously enhanced the hydrogen dissociation at the interface with the LaNi₅ film, the dominant factor for the reaction rate in the film should be proton diffusion. Thus, the highly responsive palladium deposited actuator, the speed of which was 100 times faster than that of the untreated sample, could be explained.

4.3 Difference between the Pd and Pt depositions

Although the n value of the palladium deposited sample was 0.64, approximately equal to that (n = 0.58) of the platinum deposition, the dominant factors in the both depositions were the hydrogen ion diffusion. On the other hand, the changing rate of the palladium deposited sample was 10 times faster than that of the platinum deposited sample,11) as shown in Figs. 2 and 3.

Fromm summarized the temperature dependent equations of the permeation/diffusion of hydrogen atoms in palladium and platinum film.4) At 300 K, the permeation/diffusion of hydrogen atoms in the palladium film was 10¹⁰ times higher than that in the platinum film. This acceleration qualitatively explained the high responsiveness of the palladium deposited sample at room temperature.

Based on the oxidation potential,15) the probability of oxygen absorption on the palladium surface should be higher than that on the platinum surface. The deceleration should decrease the apparent hydrogen permeation rate from 10¹⁰ to 10¹ times faster than that of the untreated sample. Therefore, both the acceleration and the deceleration determined the actuator responsiveness of the palladium deposited film.

The dominant factor was the hydrogen ion permeability through platinum thin film, because the responsiveness of the film actuator deposited by platinum was lower than that by palladium. If the highest responsiveness was obtained for the palladium deposited LaNi₅ film actuator, the dominant factor in the palladium deposition should be the hydrogen ion diffusion in LaNi₅ film. The rate determining reaction after the palladium deposition was no longer the dissociation of hydrogen gas molecules on the sample surface, but the hydrogen diffusion in the LaNi₅ film of 125 μm (1.25 × 10⁻⁴ m) thick, rather than the hydrogen permeability through the palladium thin film of 75 nm (7.5 × 10⁻⁸ m) thick.

5. Conclusion

In summary, a palladium deposited LaNi₅ alloy thin film unimorph actuator with a high responsiveness was developed. The effects of a palladium surface deposition on the mechanical response of the actuator deposited on polynimide substrates were investigated. In the experiments, the induction period of the actuation after hydrogen gas exposure was reduced from 100 s to 1 s by the palladium surface deposition. This significantly modified mechanical response is attributed to a switching of the reaction rate determining steps. The reaction order, n value for the palladium deposited LaNi₅ thin film was 0.64, which was approximately equal to that of the platinum deposition. A palladium thin film of 7.5 × 10⁻⁸ m in thickness enhanced the dissociation rate of the hydrogen gas molecules at the interface. The dissociation of the hydrogen gas molecules on the sample surface is thought to have changed to a permeation/diffusion of the hydrogen atoms into the film by means of the palladium deposition. Therefore, the rate dominant factor of the palladium deposited LaNi₅ thin film should be the activation energy of hydrogen ion diffusion. Furthermore, we concluded that an additional cause of the high responsiveness induced by palladium deposition was the hydrogen migration rate in the palladium film at room temperature. Since this actuator could be reversibly driven by hydrogen pressure control, this actuator should be useful as a sensor and/or controller of hydrogen gas flux in various hydrogen related devices.

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REFERENCES