High Responsiveness Induced by Palladium Deposition on Thin Film Actuator of LaNi₅ Hydrogen Storage Alloy*¹

Yoshitake Nishi^{1,*2}, Haru-Hisa Uchida² and Takamitsu Honjo^{1,*3}

¹Department of Materials Science, TOKAI University, Hiratsuka 259-1292, Japan

²Department of Human Development, TOKAI University, Hiratsuka 259-1292, Japan

The unimorph actuator of the LaNi₅ 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 the LaNi₅ film for the palladium deposited sample. It was also suggested that the high permeability of hydrogen in palladium film at room temperature resulted in the high responsiveness.

(Received August 20, 2004; Accepted November 22, 2004)

Keywords: actuator, unimorph structure, palladium, LaNi₅, hydrogen storage alloy, thin film

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.¹⁾ The LaNi₅ 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.²⁾ This high-volume expansion of the LaNi₅ hydrogen storage alloy generates a tremendous force, indicated by the plastic deformation of a thick-walled 18-8 stainless steel reaction cell.³⁾ 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 LaNi₅ alloy film.⁴⁾ A hydrogen storage La-Ni alloy film, prepared by flash evaporation has shown a reversible shape change on hydrogen absorption and desorption.⁴⁾ In previous works, the LaNi₅ 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 LaNi₅ alloy films deposited with more disordered crystal structure.⁹⁾ In such case we expect a long lifetime for a new actuator driven by a LaNi₅ alloy thin film. In order to apply this material to a practical actuator in the field of hydrogen energy systems, the composition dependence¹⁰⁾ and load dependence³⁾ of the strain produced by a shape change have been studied for the LaNi₅ 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⁾ 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 LaNi₅ film with palladium in order to investigate its effects on the shape change responsiveness of this new unimorph structural actuator.

2. Experimental Procedure

LaNi₅ 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 H₂ gas (7N); the resulting powder was sieved to obtain a mean grain size of 35 μm ($3.5 \pm 1.0 \times 10^{-5}$ 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±x} 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±0.1}. The crystal structure was confirmed by X-ray diffraction (TF XRD; X' Part MRD, Philips). X-ray diffraction revealed that the deposited LaNi₅ film has an amorphous structure.

To enhance the responsiveness of the LaNi_{5±0.1} unimorph actuator film, a palladium deposition was performed by ion-

*¹This Paper was Presented Spring Meeting, of The Japan Institute of Metals, held in Tokyo, on April 1, 2004.

*²Corresponding author, E-mail: am026429@keyaki.cc.u-tokai.ac.jp

*³Undergraduate Student, TOKAI University

sputtering (E1010, Hitachi Science Systems Ltd). A palladium thin film of 75 nm (7.5×10^{-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 H₂ (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. The activated unimorph actuator was then transported to a reaction bed made of silica glass. After an evacuation to desorb any remaining hydrogen, the change in material shape under different hydrogen gas pressures from 0.12 to 0.3 MPa was monitored for 10^5 s of operation time by a video recorder.^{10,11)}

The movable strain (ε^i) of the actuator was calculated using eqs. (1) & (2) taking the radius of curvature (ρ) at the mid point and a half thickness (η^i) of the bending sample.^{10,11)} The ρ value was set to be equal to the distance between the interface and the exterior of the sample, while η^i was defined as the substrate thickness.

$$\varepsilon^i = \eta^i / \rho. \quad (1)$$

The strain difference ($\Delta\varepsilon^i$) yielded by the shape change of the hydrogen storage alloy unimorph structure before and after hydrogen gas absorption was defined as eq. (2).

$$\Delta\varepsilon^i = \varepsilon^i - \varepsilon_0^i \quad (2)$$

Here, ε_0^i was the initial strain before the first hydrogen absorption in the glassy reaction tube. As indicators of actuator responsiveness, the initial rate of the shape change ($d\Delta\varepsilon^i/dt$) and the starting time of the shape change (t_i) were defined. The ($d\Delta\varepsilon^i/dt$) value was taken to be the mean rate of shape change for times less than 500 s, whereas the (t_i) value was defined as the time at a strain of 10^{-6} .

3. Results

Figure 1 shows optical photographs of the test device with (a) the untreated and (b) the palladium deposited LaNi₅ hydrogen storage alloy film unimorph structural actuator on the polyimide substrate exposed to hydrogen under a pressure of 3.0×10^5 Pa at 300 K for different reaction times. The actuator's curved shape was caused by expansion from the deposition prior to hydrogenation. The shape change was induced by the hydrogenation generated by a high hydrogen gas pressure. On the other hand, a low hydrogen gas pressure produced a dehydrogenation. Thus, a reversible change of shape was observed.

To confirm that the shape change was caused by a volume expansion of the LaNi₅ storage alloy due to hydrogen absorption, the shape change was observed under two different experimental conditions. The shape change did not occur for a plain polyimide substrate under a hydrogen gas atmosphere and for the new thin-film actuator under a helium gas atmosphere. Thus, we concluded that the actuator's shape change was driven by a hydriding expansion of the LaNi₅ alloy thin film operated by gas pressure.

Fig. 1 Optical photographs of the test device with untreated (a) and Pd-deposited (b) hydrogen storage alloy film exposed to hydrogen at a pressure of 3.0×10^5 Pa at 300 K for different reaction times.

On the other hand, pulverization and fatigue fracture are serious problems to apply to practical actuators. Fine LaNi₅ particles, smaller than 10^{-6} m diameter, did not exhibit any fractures after a large number ($>10^6$) of hydriding/degassing cycles.⁶⁾ If the thin film less than 10^{-6} m thick was prepared, it is difficult the fracture is to be induced. Based on SEM observations, cracking and peeling were not readily seen on the actuator surface after hydriding and dehydriding. In addition, no cracks were observed in the LaNi₅ thin film during a fatigue test of more than 100 cycles.

Figure 1(a) shows the shape changes of the untreated sample operated from 0 to 10^5 s. Although a large change was not found in the operated sample below 10^3 s such a change was noticed from 10^3 to 10^5 s. Shape changes in the palladium deposited sample operated from 0 to 10^3 s also took place, as shown in Fig. 1(b), with a large shape change occurring from 100 to 10^3 s. From the results presented in Fig. 1, we concluded that the palladium deposition greatly enhanced the shape change rate on hydriding. This high responsiveness should appeal to a broad market.

In order to evaluate the shape change quantitatively, the $\Delta\varepsilon^i$ values were estimated by using eqs. (1) and (2). Figure 2 shows the relationship between the reaction time, t , after exposure to hydrogen under 1.2×10^5 Pa, and the strain generated by the shape change, $\Delta\varepsilon^i$, of the unimorph structural film device with and without a palladium deposition. The initiating time (incubation period) for the actuation to be measured after hydrogen gas exposure was 100 s for the

Fig. 2 Relationship between reaction time, t , after exposure to hydrogen under 1.2×10^5 Pa, and strain generated by shape change, $\Delta\epsilon^i$, of the device with a Pd-deposited LaNi₅ hydrogen storage alloy film (solid line), together with Pt-deposited (dotted line) and untreated (broken line) samples.

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.

$$V = dN_{H_2}/dt = k \times P^n \times \exp(-A/RT) \quad (3)$$

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 LaNi₅ 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, ($d\Delta\epsilon^i/dt$), is equal to the hydrogen absorbed rate (dN_{H_2}/dt), the value of $d\Delta\epsilon^i/dt$, at a constant temperature, could be expressed by the following equation.

$$d\Delta\epsilon^i/dt \propto dN_{H_2}/dt \propto P^n \quad (4)$$

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, $d\Delta\epsilon^i/dt$, of the hydrogen storage LaNi₅ alloy film with and without palladium deposition.

The n value was equal to one for the untreated LaNi₅ thin

Fig. 3 Relationship between the applied hydrogen pressure, P_{H_2} , and rate of strain generated by shape change, $d\Delta\epsilon^i/dt$, of the device with a Pd-deposited LaNi₅ hydrogen storage alloy film (solid line), together with Pt-deposited (dotted line) and untreated (broken line) samples.

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 LaNi₅ 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 LaNi₅ thin film, as shown in Fig. 3. The palladium deposition, which formed a palladium thin film of 75 nm (7.5×10^{-8} 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 μm (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.¹⁴⁾ At 300 K, the permeation/diffusion of hydrogen atoms in the palladium film was 10^{10} 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 10^{10} to 10^2 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 polyimide 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.

Acknowledgement

Author would like to thank Associate Prof. Dr. Y. Matsumura, Dr. H. Yabe, Mr. N. Okada and Mr. K. Numazaki for their useful helps.

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