An Improved H₂-Gas Pressure Operated LaNi₅ Powder-Dispersed Polyurethane/Titanium 2-Layer Actuator with Reversible Giant and Rapid Expansion by Hydrogenation

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A unimorph 2-layer (PU:LaNi₅/Ti) actuator consisting of a driving composite sheet with large expansion of polyurethane (PU) dispersed with powder mixture of hydrogen storage alloy of 35 vol%-LaNi₅ and Pd-Al₂O₃ catalyst prepared by solution cast method, and a 5 μ m thick Ti sheet exhibited reversible and giant rapid bending motion when subjected to hydrogen atmosphere. Reversible motion was achieved below 0.20 MPa-H₂ pressure where maximum strain (ϵ^{max}) values on vertical and horizontal directions were more than 2400 and 1800 ppm, respectively about 1.6 times larger than that reported (1520 and 1120 ppm) for the same actuator PU:LaNi₅/Cu with 10 μ m thick copper (Cu) sheet. Moreover, the maximum responsiveness ($d\epsilon/dt$)^{max} by hydrogenation of cyclic motion of the PU:LaNi₅/Ti was higher than that of the PU:LaNi₅/Cu. The increased ($d\epsilon/dt$)^{max} values mostly corresponded to decreasing elastic load resistivity ($dF/d\epsilon$). These were due to Ti having higher stiffness and strength than Cu allowing thinner 5 μ m sheet. Caution for safety is advised since values presented herein may be different when applying the actuator to zero gravity environments. [doi:10.2320/matertrans.M2017212]

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1. Introduction

Actuators driven reversibly by hydrogen gas pressure are aimed to be applied as hydrogen flux controllers or sensors in hydrogen powered engines, energy harvesters and other devices contributing to clean energy on Earth or in space. Recently, H₂ gas powered actuators based on hydrogen storage alloy LaNi₅ with its tremendous volume expansion of 25 Vol%, and strong power when subjected to hydrogenation under atmospheric pressure have been gaining attention.^{1–4)}

Early research has centred around LaNi₅ thin films deposited on polymers.^{2–4)} In a 2-layer unimorph actuator of driving side of <1 μ m LiNi₅ film deposited on polyimide (PI) substrate, sputtering platinum (Pt) on the LiNi₅ side (Pt-LaNi₅/PI) reduced initial response time from 100 to 10 s producing no damage to LiNi₅ film while increasing bending motion strain counter to gravity, $\Delta\epsilon$ at $t = 1000$ s by a factor of two.²⁾ Replacing Pt with palladium (Pd) reduced initial response time to 1 s, raising $\Delta\epsilon$ of (Pd-LaNi₅/PI) at $t = 1000$ s to 900×10^{-6} .³⁾ Subsequent research replacing polymer PI layer with 10 μ m Cu foil (Pd-LaNi₅/Cu)⁴⁾ is reported to increase $\Delta\epsilon$ at $t = 50$ s to nearly 500×10^{-6} , over those of (Pd-LaNi₅/PI), (Pt-LaNi₅/PI), and (Untreated-LaNi₅/PI) at $\sim 350 \times 10^{-6}$, 300×10^{-6} and $\sim 25 \times 10^{-6}$ strains, respectively.^{2–4)}

However, Cu being a soft metal resulted in tight coiling of the (Pd-LaNi₅/Cu) actuators at higher H₂ exposure times from $t = 100$ to 1000 s. The coiling was not perfectly reversible due to work hardening of the Cu foil creating plastic deformation.⁴⁾ Coil motion has been reported in other actuators

as well such as commercially provided Ni-Ti shape memory alloy.⁵⁾ Hence other research has focused on thicker substrate and driving side. For example, since H₂ has sufficient permeability in polymers, 2-layer actuators (SR:LaNi₅/SR) consisting of two 500 μ m thick silicon rubber (SR) elements have been suggested: a driving SR sheet dispersed with LaNi₅ powder adhered to supporting pure SR thick sheet or rod.^{6–8)} However desired high responsiveness of soft polymer dispersed with LaNi₅ alone is not achieved.^{6–8)} An addition of Pd-Al₂O₃ catalyst to the LaNi₅ powder prior to dispersion in polymer has enhanced the responsiveness as well as motion strain.⁹⁾

Stiffness has been improved in 2-layer actuators (PU:LaNi₅/PU)¹⁰⁾ where both layers are 500 μ m thick polyurethane (PU): the driving PU layer dispersed with (35 vol%) LaNi₅-Pd-Al₂O₃ mixture prepared by solution cast method. The PU:LaNi₅/PU¹⁰⁾ actuators take advantage of both high elasticity as well as high limit value of elastic strain of PU where geometry and mixed ratio [PU]-[LaNi₅-Pd-Al₂O₃] are easily controlled.¹⁰⁾

The PU:LaNi₅/PU as well as SR:LaNi₅/SR are reported to achieve more than 2000 ppm ϵ_{max} value of reversible cyclic bending motion in vertical direction in 0.20 MPa-H₂ gas.⁹⁾ However, when rotated 90 deg for horizontal motion both PU:LaNi₅/PU¹⁰⁾ and SR:LaNi₅/SR⁹⁾ sag with spontaneous bending due to gravity the horizontal motion not attained.¹¹⁾

On the other hand, research of replacing PU substrate with 10 μ m thick Cu for PU:LaNi₅/Cu¹¹⁾ actuator successfully achieved reversible bending motion, ϵ_{max} of more than 1520 and 1120 ppm on vertical and horizontal directions, respectively in 0.20 MPa-H₂ gas atmosphere. However, the

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tradeoff is its vertical $\varepsilon_{\max}$ of 1500 ppm is less than those of PU:LaNi₅/PU¹⁰⁾ and SR:LaNi₅/SR.⁹⁾

To solve these problems we fabricate PU:LaNi₅/Ti actuator using thinner 5 μ m titanium (Ti) sheet since Ti has high stiffness and strength. We demonstrate reversible bending motion, $\varepsilon_{\max}$ in vertical and horizontal directions in PU:LaNi₅/Ti can be raised 60% over that of PU:LaNi₅/Cu¹¹⁾ by Ti. Moreover, we show maximum responsiveness $(d\varepsilon/dt)^{\max}$ by hydrogenation of cyclic motion of the PU:LaNi₅/Ti will be higher than that of the PU:LaNi₅/Cu¹¹⁾.

2. Experimental Procedure

2.1 Sample preparation

The unimorph sheet of PU:LaNi₅/Ti was constructed with the supporting titanium (Ti) thin sheet of 5 μ m thickness with high specific stiffness (apparent hardening modulus per specific weight) adhered to a driving polyurethane (PU) composite dispersed with powders mixture of LaNi₅ hydrogen storage alloy (35 vol%) and Pd-Al₂O₃ catalyst powders were prepared by solution cast method.¹⁰⁾

The sample LaNi₅ alloys pulverized under argon gas atmosphere were sieved to obtain a grain size of less than 100 μ m in diameter. The chemical composition was analyzed by energy dispersive X-ray spectroscopy (EDS: EMAX-5770, HORIBA) as LaNi_{5.2}. Pd (5 mass%)-Al₂O₃ powders with 1 to 10 μ m in diameter were mixed to the LaNi₅ hydrogen storage alloy powders before dispersing in the PU solution.^{9,10)}

Driving sheet was PU (Estane Company, 58888 NAT 021) composite dispersed with hydrogen storage alloy powders, which was mixed with Pd (5 mass%) - Al₂O₃ powders to enhance the responsiveness. The simple solution cast method for the PU:LaNi₅ composite driving sheet was as follows. 1.8 g of PU granules were dissolved in about 36 ml of N, N-dimethylformamide (DMF) at 348 K for 130 min. LaNi₅ (2.05 g) and Pd-Al₂O₃ (0.191 g) powders were added during solution stirring at constant temperature for 10 min. Then, the mixed solution was poured onto a glass plate and dried at 333 K under atmospheric pressure for 21 h to make the composite PU. The obtained films were removed from the plate with the help of ethanol. Then, it was put into a ventilated oven at 403 K for 4 h drying, in order to eliminate residual solvent. The finished PU:LaNi₅ driving sheet sizes of length, width and thickness were 40, 10 and 0.5 mm, respectively, with thickness variation of ± 0.01 mm. All sheets were formed using a mold. The adhesion of the PU:LaNi₅ driving sheet with 5 μ m thick Ti sheet was performed after 20 h from start point of drying and just one hour before finish point of solidification. After that, it was cut to the unimorph sample form.

Finally, the movements of the samples were observed alternately introducing 0.2 MPa-H₂ gas and evacuating to vacuum, where the evacuation was carried out within 5 s using a mechanical rotary pump. Tests were done starting from both vertical and horizontal positions to obtain motion strain, ε and responsiveness, $(d\varepsilon/dt)$.

2.2 Estimation of motion strain

The sample was activated in a transparent glass-made

drive evaluation apparatus under H₂ pressure of 0.20 MPa and 0.30 MPa. Based on the shape change of the sample obtained in pictures captured by a VTR camera, the radius of curvature was obtained for the evaluation. The bending mover strain (ε) of the actuator was calculated using eq. (1).

$$\varepsilon = \eta/\rho \quad (1)$$

Here, η and ρ are assumed to be half thickness of unimorph sample and radius of curvature at sample longitudinal centerline, respectively. Shape change was measured before and after hydrogen gas absorption for 10 cycles.

3. Results

3.1 Reversibility of bending motion

Figure 1 compares motion strain, ε vs. time, t graphs for our unimorph PU:LaNi₅/Ti actuator with those of the literature.^{9–11)} At room temperature although cyclic bending motion is irreversible at H₂ pressure of 0.3 MPa, the reversible cyclic bending motion is achieved at 0.2 MPa. The cyclic bending motion occurs with alternating H₂ pressure $\leftrightarrow$ vacuum cycles. Reported values under the same conditions for PU:LaNi₅/PU¹⁰⁾, SR:LaNi₅/SR⁹⁾, ABS:LaNi₅/ABS¹⁰⁾ and PU:LaNi₅/Cu¹¹⁾ unimorphs are shown.

3.2 Reversible bending motion from vertical and horizontal positions

Figure 2 shows the optical photographs of the mover unimorph sheet of PU:LaNi₅/Ti from the initial vertical and horizontal positions respectively before (dark dotted lines), and after hydrogenation under 0.2 MPa-H₂ gas pressure (light dotted lines) for $t = 10$ ks. Note for the horizontal set shown in Fig. 2, the Ti-stiffened PU:LaNi₅/Ti actuator maintains at initial horizontal position counter to gravity before hydrogenation, improved from the sagging in the form of

Fig. 1 Cyclic changes in bending strain of reversible and irreversible motion (ε) from vertical position of unimorph sheets of PU:LaNi₅/PU¹⁰⁾, SR:LaNi₅/SR⁹⁾ and ABS:LaNi₅/ABS¹⁰⁾ against hydrogenation time, t (ks) under 0.2 and 0.3 MPa-H₂, together with our PU:LaNi₅/Ti sheet of driving Pu-LaNi₅ composite supported by titanium film (5 μ m thickness).

spontaneous bending reported for SR:LaNi₅/SR⁹⁾, PU:LaNi₅/PU¹⁰⁾ and ABS:LaNi₅/ABS¹⁰⁾.

This sample is bended from base point line to maximum strain movement, $\varepsilon_{\max}$ after 10³ s hydrogenation as shown in Fig. 2. The PU:LaNi₅/Ti sheet shows remarkable large bending motion by hydrogenation due to volume expansion by the LaNi₅ powders in the driving sheet.

Figure 3 shows reversible motion of our PU:LaNi₅/Ti unimorph actuator is successfully achieved in both vertical and horizontal positions. The plot shows changes in bending strain (ε) of reversible motion from initial vertical and horizontal positions to $\varepsilon_{\max}$ of PU:LaNi₅/Ti after alternating exposure to 0.2 MPa-H₂ and vacuum against reaction time; t . The first hydrogenation for 3 h (more than 10 ks) from the horizontal position of the PU:LaNi₅/Ti sheet induces the large maximum strain from 1650 ppm, which is smaller than that (2400 ppm in Fig. 3) at vertical set. The first evacuation is also observed to reverse perfectly. Since the residual strain in the form of sagging in horizontal position cannot be detected under evacuation, the cyclic reversible motion of

Fig. 2 Optical photographs of mover unimorph sheet of PU:LaNi₅/Ti at vertical and horizontal initial and maximum positions before and after H₂ gas pressure of 0.20 MPa at 10 ks.

Fig. 3 Cyclic changes in bending strain (ε) of reversible motion at vertical and horizontal sets of unimorph sheet of PU:LaNi₅/Ti of driving composites distributed with mixed ratio of LaNi₅ powders at 35 vol%LaNi₅ supported by titanium film (5 μ m thickness) after exposure to hydrogen gas under 0.2 MPa-H₂ and to vacuum, against reaction time; t .

PU:LaNi₅/Ti is operated from the 1st hydrogenation and 1st evacuation under the 0.2 MPa-H₂ gas pressure. Data for time exposure to H₂ gas always starts from vacuum; whereas data for time exposure to vacuum always starts from 0.2 MPa-H₂ gas atmosphere.

3.3 Bending motion strain vs. hydrogenation and evacuation holding times for vertical and horizontal positions

Figure 4 shows bending motion strain, ε vs. holding time, t (ks) for vertical and horizontal positions: hydrogenation and evacuation of PU:LaNi₅/Ti. When the 0.2 MPa H₂ pressure, or vacuum is held constant, the data exhibit exponential growth and decay respectively.

Figure 4 (a) shows for time exposure of 0.2 MPa-H₂ gas pressure, motion strain, ε saturates at the high value of $\varepsilon_{\max} = 2400$ ppm after 0.5 ks maintaining without decay after 10 ks. This curve represents all vertical sets tested from 1st to 10th cycle (Fig. 2 top and Fig. 3).

Fig. 4 Changes in bending motion strain (ε) at vertical and horizontal sets of unimorph sheet of PU:LaNi₅/Ti after 0.2 MPa hydrogenation (a); and evacuation (b) against reaction time, t for the first 10 cycles. (a) Exposure to hydrogen, (b) Exposure to vacuum.

Figure 4 (a) also shows for all horizontal sets tested from 2nd to 10th cycle (Fig. 2 bottom), the ε saturates quickly at the high value of $\varepsilon^{max} = 1800$ ppm after about 1 ks maintaining without decay after 10 ks. However, during the 1st cycle of H₂ exposure horizontal strain motion is delayed exhibiting near saturation strain at 1700 ppm at 10 ks. This is expected since H₂ takes time to permeate into PU.

On the other hand, Fig. 4 (b) shows for evacuation to vacuum carried out within 5 s (see Experimental), all vertical sets tested from 1st to 10th cycle (Fig. 2 top), motion strain, ε decays rapidly to the low value of ~ 80 ppm after 0.50 ks. Note abscissa time axis in Fig. 4(b) is expanded to illustrate rapid decay. Figure 4 (b) also shows for all horizontal sets tested from 1st to 10th cycle (Fig. 2 top), ε decays rapidly to the low value of ~ 230 ppm after 0.50 ks, and to ~ 170 ppm after 1.0 ks. With the exception of the 1st horizontal set for hydrogenation, the $(d\varepsilon/dt)$ in Figs 4(a) and (b) of 1st to 10th cycles are nearly identical as can be seen in Figs. 1 and 3.

The exponential nature of ε vs. t curves shapes appear to represent kinetics equations.

4. Discussion

4.1 Influence of supporting sheet from Cu to Ti on ε^{max} at horizontal and vertical sets of unimorph sets

As shown in Figs. 3 and 4, cyclic changes in bending strain (ε) at horizontal set of unimorph sheet of PU:LaNi₅/Ti after exposure to hydrogen under 0.2 MPa-H₂ and to vacuum have been illustrated against reaction time (t). The maximum strain (ε^{max}) on vertical and horizontal directions of the PU:LaNi₅/Ti and PU:LaNi₅/Cu⁽¹¹⁾ are summarized in Table 1. The maximum bending strain (ε^{max}) (1750 ppm) at horizontal set (PU:LaNi₅/Ti:Horizontal) is lower than that (2450 ppm) at vertical set (PU:LaNi₅/Ti:Vertical).

$$\begin{aligned}\varepsilon^{max}(\text{PU:LaNi}_5/\text{Ti:Vertical}) &= 2450 \text{ ppm} \\ &= \varepsilon^{max}(\text{PU:LaNi}_5/\text{Ti:Horizontal}) + 700 \text{ ppm} \quad (2) \\ &= 1750 + 700 \text{ ppm}\end{aligned}$$

Although the set conversion from vertical to horizontal decreases ε^{max} to 1750 ppm, the 1750 ppm for either vertical or horizontal movement is considered large enough to utilize for practical articles.

For PU:LaNi₅/PU⁽¹⁰⁾, on the other hand, reversible motion

in horizontal direction cannot be obtained due to bending relaxation of the thicker 500 μm PU:LaNi₅ composite driving sheet. Decreasing the ε^{max} value by the set conversion from vertical to horizontal probably depends on the initial bending strain with respect to gravity. Since the bending resistivity of the composites can be enhanced by using the titanium substrate, the high ε^{max} value of 1750 ppm is obtained at horizontal set (PU:LaNi₅/Ti:Horizontal).

The maximum strain (ε^{max}) (2450 and 1750 ppm) on vertical and horizontal directions, respectively, of the PU:LaNi₅/Ti are 1.61 and 1.56 times larger than those (1520 and 1120 ppm)⁽¹¹⁾ of the PU:LaNi₅/Cu described above.

$$\begin{aligned}\varepsilon^{max}(\text{PU:LaNi}_5/\text{Ti:Vertical}) &= 2450 \text{ ppm} \\ &= 1.61 \times \varepsilon^{max}(\text{PU:LaNi}_5/\text{Cu:Vertical}) \quad (3) \\ &= 1.61 \times 1520 \text{ ppm}\end{aligned}$$

$$\begin{aligned}\varepsilon^{max}(\text{PU:LaNi}_5/\text{Ti:Horizontal}) &= 1750 \text{ ppm} \\ &= 1.56 \times \varepsilon^{max}(\text{PU:LaNi}_5/\text{Cu:Horizontal}) \quad (4) \\ &= 1.56 \times 1120\end{aligned}$$

It is mostly caused by the thinner, stiffer and lighter 5 μm Ti supporting sheet over that of the 10 μm Cu sheet.

4.2 Influence of supporting sheet from polymer to Ti on ε^{max} at vertical set of unimorph sets

As shown in Fig. 1, although the bending motion from the vertical position of PU:LaNi₅/Ti operated by hydrogenation at 0.3 MPa H₂ gas is irreversible, at 0.2 MPa H₂ pressure reversible motion is attained. Reversible motion is also reported in PU:LaNi₅/Cu⁽¹¹⁾, PU:LaNi₅/PU⁽¹⁰⁾, SR:LaNi₅/SR⁽⁹⁾ and ABS:LaNi₅/ABS.⁽¹⁰⁾ Their vertical and horizontal parameters are summarized in Table 1.

The vertical ε^{max} of 2450 ppm of PU:LaNi₅/Ti is slightly and tremendously higher than that (2300 and 250 ppm) reported for PU:LaNi₅/PU⁽¹⁰⁾ and ABS:LaNi₅/ABS⁽¹⁰⁾, respectively, although it is slightly lower than that (2500 ppm) of the SR:LaNi₅/SR.⁽⁹⁾

$$\begin{aligned}\varepsilon^{max}(\text{PU : LaNi}_5/\text{Ti}) &= \varepsilon^{max}(\text{PU : LaNi}_5/\text{PU}) \\ &\quad + 150 \text{ ppm} \quad (5)^{(10)}\end{aligned}$$

$$\begin{aligned}\varepsilon^{max}(\text{PU:LaNi}_5/\text{Ti}) &= \varepsilon^{max}(\text{SR:LaNi}_5/\text{SR}) \\ &\quad - 50 \text{ ppm} \quad (6)^{(9)}\end{aligned}$$

Table 1 The maximum reversible strain (ε^{max}) and responsiveness ($d\varepsilon^{max}/dt$) in vertical direction, as well as elastic load resistivity ($dF/d\varepsilon$) and elasticity ($d\sigma/d\varepsilon$) of the PU:LaNi₅/Ti along with those reported for PU:LaNi₅/Cu⁽¹¹⁾, PU:LaNi₅/PU⁽¹⁰⁾, ABS:LaNi₅/ABS⁽¹⁰⁾ and SR:LaNi₅/SR⁽⁹⁾, together with ε^{max} on horizontal direction of the PU:LaNi₅/Ti and PU:LaNi₅/Cu,⁽¹¹⁾ as well as elasticity of Pd⁽¹³⁾ and Al₂O₃⁽¹²⁾.

	ε^{max} (ppm)	$(d\varepsilon/dt)^{max}$ (s ⁻¹)		$dF/d\varepsilon$	$d\sigma/d\varepsilon$
	(0.2 MPaH ₂)	(0.2 MPaH ₂)	Evacuation		
PU:LaNi ₅ /Ti	2450	950	600	900 N	175 MPa
PU:LaNi ₅ /Cu	1520	300	300	1460 N	210 MPa
PU:LaNi ₅ /PU	2300	700	350	1400 N	140 MPa
ABS:LaNi ₅ /ABS	250	30	50	2000 N	385 MPa
SR:LaNi ₅ /SR	2500	1250	800	200 N	40 MPa
PU:LaNi ₅ /Ti (Horizontal)	1750				
PU:LaNi ₅ /Cu (Horizontal)	1120				
Pd					117 GPa
Al ₂ O ₃					390+/-10 GPa

$$\varepsilon^{max}(\text{PU:LaNi}_5/\text{Ti}) = \varepsilon^{max}(\text{ABS:LaNi}_5/\text{ABS}) + 2200 \text{ ppm} \quad (7)^{10}$$

The maximum bending strain (ε^{max}) of reversible motion of the unimorph sheet strongly depends on not only hydrogenation expansion of LaNi₅ powders, but also both elasticity and its limits of the composites. Thus, the bending stress-strain curves have been obtained. Since the thin Ti sheet probably exhibits the high stiffness and small area of cross section, the driving force generated by hydrogen storage alloy powder concentrates to the bending force, rather than the length expansion.

4.3 Responsiveness ($d\varepsilon/dt$) of reversible bending motion induced by alternating hydrogenation and evacuation

Table 1 exhibits the maximum values of responsiveness ($d\varepsilon/dt$)^{max} of reversible bending motion at vertical and horizontal sets, respectively of PU:LaNi₅/Ti for the alternating hydrogenation and evacuation, together with those of vertical sets reported for PU:LaNi₅/PU¹⁰, SR:LaNi₅/SR⁹ and ABS:LaNi₅/ABS¹⁰ sheets, respectively.

By implementing use of thin Ti foil as substrate in the PU:LaNi₅/Ti the maximum responsiveness ($d\varepsilon/dt$)^{max} generated by hydrogenation in the vertical set of PU:LaNi₅/Ti reaches 950 ppm ks⁻¹, improved 1.36, 3 and 32 times higher than those reported for PU:LaNi₅/PU, PU:LaNi₅/Cu and ABS:LaNi₅/ABS at 700, 300 and 30 ppm ks⁻¹, respectively.^{10,11} However, the ($d\varepsilon/dt$)^{max} is apparently 32% lower than that of the SR:LaNi₅/SR.⁹

$$\begin{aligned} (d\varepsilon/dt)^{max}(\text{SR:LaNi}_5/\text{SR}) &= 1250^9 \\ > (d\varepsilon/dt)^{max}(\text{PU:LaNi}_5/\text{Ti}) &= 950 \\ > (d\varepsilon/dt)^{max}(\text{PU:LaNi}_5/\text{PU}) &= 700^{10} \\ > (d\varepsilon/dt)^{max}(\text{PU:LaNi}_5/\text{Cu}) &= 300^{11} \\ > (d\varepsilon/dt)^{max}(\text{ABS:LaNi}_5/\text{ABS}) &= 30^{10} \end{aligned} \quad (8)$$

Likewise, Table 1 shows ($d\varepsilon/dt$)^{max} generated by evacuation in vertical set of PU:LaNi₅/Ti reaches 600 ppm ks⁻¹, improved 1.36, 3 and 32 times higher than those reported for PU:LaNi₅/PU, PU:LaNi₅/Cu and ABS:LaNi₅/ABS at 350, 300 and 50 ppm ks⁻¹, respectively.^{10,11} However, the ($d\varepsilon/dt$)^{max} is apparently 33% lower than that of the SR:LaNi₅/SR.⁹

$$\begin{aligned} (d\varepsilon/dt)^{max}(\text{SR:LaNi}_5/\text{SR}) &= 800^9 \\ > (d\varepsilon/dt)^{max}(\text{PU:LaNi}_5/\text{Ti}) &= 600 \\ > (d\varepsilon/dt)^{max}(\text{PU:wLaNi}_5/\text{PU}) &= 350^{10} \\ \geq (d\varepsilon/dt)^{max}(\text{PU:LaNi}_5/\text{Cu}) &= 300^{11} \\ > (d\varepsilon/dt)^{max}(\text{ABS:LaNi}_5/\text{ABS}) &= 50^{10} \end{aligned} \quad (9)$$

The maximum responsiveness ($d\varepsilon/dt$)^{max} of the PU:LaNi₅/Ti at vertical set for 100 s is about 20% and 50% higher than that at horizontal set by hydrogenation and evacuation, respectively.

On the contrary, the ($d\varepsilon/dt$)^{max} values of the PU:LaNi₅/Ti at horizontal set at 2nd to 10th for short time less than 10 s is about 3 times higher than that at vertical set by hydrogenation, although the ($d\varepsilon/dt$)^{max} value of the PU:LaNi₅/Ti at horizontal set at the 1st hydrogenation for short time less than 10 s is approximately equal to that at vertical set by hydrogenation.

Although the ($d\varepsilon/dt$)^{max} value, generated by hydrogenation of the PU:LaNi₅/Ti, is 25% lower than that of the SR:LaNi₅/SR sheet, it is 25% higher than of that of the PU:LaNi₅/PU sheet.

Although the perfect reversible motion cannot be found for ABS:LaNi₅/ABS unimorph sheet under 0.2 MPa H₂ gas, the hydrogenation ($d\varepsilon/dt$)^{max} value of the PU:LaNi₅/Ti sheet is about 35 times higher than that of the ABS unimorph sheet.

When both hydrogenation power (dF/dC) and hydrogenation rate (dC/dt) are defined, the responsiveness ($d\varepsilon/dt$), which strongly inversely corresponds to elastic load resistivity ($dF/d\varepsilon$), is expressed by the following equation:

$$\begin{aligned} (d\varepsilon/dt) &= (dF/dt)/(dF/d\varepsilon) \\ &= (dC/dt)(dF/dC)/(dF/d\varepsilon) \end{aligned} \quad (10)$$

Based on former work, the absorption rate (dC/dt) is generally dominated at interface of LaNi₅ film.³ On the other hand, the dC/dt value of Pd coated LaNi₅ mover film has been controlled by diffusion in bulk.³ Since the Pd, which acts as a catalyst, decreases activation energy of hydrogen gas absorption at interface, it enhances the responsiveness ($d\varepsilon/dt$).³ When the volume fraction of LaNi₅ powders is 35 vol% in the composites, the responsiveness ($d\varepsilon/dt$) of bending motion of the PU:LaNi₅/Ti sheet is assumed to be dominated by the hydrogenation expansion power (dF/dC) and elastic load resistivity ($dF/d\varepsilon$), which is induced by sheet thickness, as well as the elasticity of composites.

4.4 Dependence of elastic load resistivity on ($d\varepsilon/dt$)^{max}

The maximum responsiveness ($d\varepsilon/dt$)^{max} doesn't perfectly depends on the elasticity ($d\sigma/d\varepsilon$). Considering with sample thickness, the elastic load resistivity ($dF/d\varepsilon$) has been obtained, as shown in Fig. 5 and summarized in Table 1.

On the other hand, the elastic load resistivity ($dF/d\varepsilon$) of PU:LaNi₅/Ti is remarkably higher than that of SR:LaNi₅/SR. The $dF/d\varepsilon$ of PU:LaNi₅/Ti is lower than that of PU:LaNi₅/PU, as well as apparently lower than that of ABS:LaNi₅/ABS. As shown in Fig. 5 and the following equation, the $dF/d\varepsilon$ values are 200, 900, 1400, 1460 and 2000 N for SR:LaNi₅/SR, PU:LaNi₅/Ti, PU:LaNi₅/PU, PU:LaNi₅/Cu and ABS:LaNi₅/ABS, respectively.

$$\begin{aligned} dF/d\varepsilon(200\text{N:SR:LaNi}_5/\text{SR}) &= 200^9 \\ \ll dF/d\varepsilon(900\text{N:PU:LaNi}_5/\text{Ti}) &= 900 \\ < dF/d\varepsilon(1400\text{N:PU:LaNi}_5/\text{PU}) &= 1400^{10} \\ \leq dF/d\varepsilon(1460\text{N:PU:LaNi}_5/\text{Cu}) &= 1460^{11} \\ \ll dF/d\varepsilon(2000\text{N:ABS:LaNi}_5/\text{ABS}) &= 2000^{10} \end{aligned} \quad (11)$$

As the case of vertical set of PU:LaNi₅/Ti in Figs. 3 and

Fig. 5 Bending load-strain curves of elastic deformation for unimorph (PU:LaNi₅/Ti) sheets of driving composites distributed with mixed ratio of LaNi₅ powders at 35 vol%LaNi₅ supported by titanium film (5 μm thickness), together with PU:LaNi₅/Cu⁽¹¹⁾, PU:LaNi₅/PU⁽¹⁰⁾, SR:LaNi₅/SR⁽⁹⁾ and ABS:LaNi₅/ABS⁽¹⁰⁾.

4, the hydrogenation enhances the maximum bending strain (ϵ^{max}), which is 2450 ppm for 500 s of hydrogenation time under 0.2 MPa H₂ gas. The subsequent evacuation for 200 s tremendously decreases the bending strain to zero. Since the residual strain is zero, this bending motion is reversible, that is, elastic deformation.

As shown in Table 1 and the following equation, the elasticity ($d\sigma/d\epsilon$) values are 40, 140, 175, 210 and 385 MPa for SR:LaNi₅/SR⁽⁹⁾, PU:LaNi₅/Ti, PU:LaNi₅/PU⁽¹⁰⁾, PU:LaNi₅/Cu⁽¹¹⁾ and ABS:LaNi₅/ABS⁽¹⁰⁾, and are much less than 390/+10 and 117 GPa for Al₂O₃⁽¹²⁾ and palladium⁽¹³⁾, respectively.

$$\begin{aligned}
 & d\sigma/d\epsilon(40\text{MPa:SR:LaNi}_5/\text{SR})^9 \\
 & < d\sigma/d\epsilon(140\text{MPa:PU:LaNi}_5/\text{PU})^{10} \\
 & < d\sigma/d\epsilon(175\text{MPa:PU:LaNi}_5/\text{Ti}) \\
 & < d\sigma/d\epsilon(210\text{MPa:PU:LaNi}_5/\text{Cu})^{11} \\
 & \ll d\sigma/d\epsilon(385\text{MPa:ABS:LaNi}_5/\text{ABS})^9 \\
 & \ll d\sigma/d\epsilon(117\text{GPa:Pd})^{13} \\
 & \ll d\sigma/d\epsilon(390 + / - 10\text{GPa:Al}_2\text{O}_3)^{12} \quad (12)
 \end{aligned}$$

The maximum responsiveness ($d\epsilon/dt$)^{max} inversely corresponds to the elastic load resistivity ($dF/d\epsilon$) as shown in Table 1. Thus, the high responsiveness ($d\epsilon/dt$)^{max} (see eqs. (9) and (10)) of the composites can be explained by the low $dF/d\epsilon$ values (see Fig. 5). Since the expansion limit can be controlled under 0.2 MPa H₂ gas pressure, the reversible motion by both hydrogenation and evacuation of mover composite with 35 vol%LaNi₅ powders dispersed in polyurethane can be obtained.

5. Conclusions

We developed a new reversibly operating unimorph

2-layer (PU:LaNi₅/Ti) actuator consisting of a driving polyurethane (PU) composite sheet dispersed with powder mixture of hydrogen storage alloy; 5 vol%-LaNi₅ and Pd-Al₂O₃ catalyst prepared by solution cast method, and a 5 μm thick Ti sheet. Taking advantage of tremendous volume expansion of hydrogen storage alloy LaNi₅ dispersed in PU, along with implementation of 5 μm high-stiffness Ti sheet, reversible and giant rapid bending motion at both vertical and horizontal positions with respect to gravity were achieved when controlled by alternating H₂ pressure - vacuum cycles.

(1) At room temperature although cyclic bending motion was irreversible at 0.3 MPa-H₂ pressure, the reversible cyclic bending motion was achieved at 0.2 MPa-H₂.

(2) The maximum strain of reversible bending motion (ϵ^{max}) of the PU:LaNi₅/Ti sheet was more than 2400 and 1800 ppm on vertical and horizontal sets, respectively. They were about 1.6 times larger than those (1520 and 1120 ppm) reported for identical actuator PU:LaNi₅/Cu with 10 μm Cu thickness. The improvements were brought about by the thinner, stiffer and lighter 5 μm Ti supporting sheet.

(3) From initial horizontal position counter to gravity, the PU:LaNi₅/Ti actuator exhibited no sagging in the form of spontaneous bending, superior to reported data of SR:LaNi₅/SR, PU:LaNi₅/PU and ABS:LaNi₅/ABS. Caution for safety is advised since values presented herein may be different when applying the actuator to zero gravity environments.

(4) Moreover, the vertical ϵ^{max} of 2450 ppm of PU:LaNi₅/Ti was slightly and tremendously higher than those (2300 and 250 ppm) reported for PU:LaNi₅/PU and ABS:LaNi₅/ABS, respectively, although it was slightly lower than that (2500 ppm) of the SR:LaNi₅/SR.

(5) The maximum responsiveness ($d\epsilon/dt$)^{max} by both hydrogenation and evacuation of cyclic motion of the PU:LaNi₅/Ti sheet were higher than that of the PU:LaNi₅/PU, PU:LaNi₅/Cu and ABS:LaNi₅/ABS, although they were lower than those of SR:LaNi₅/SR. Increasing ($d\epsilon/dt$)^{max} values mostly corresponded to decreasing the elastic load resistivity ($dF/d\epsilon$).

(6) The maximum bending strain (ϵ^{max}) of reversible motion of the unimorph sheet strongly depended on not only hydrogenation expansion of LaNi₅ powders in PU, but also both elasticity and its limits of the PU-powder composites. Thus, the bending stress-strain curves were obtained. Since the thin Ti sheet probably exhibited high stiffness and small cross sectional area, the driving force generated by hydrogen storage alloy powder concentrates on bending force, rather than length expansion.

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REFERENCES

- 1) J.J.G. Willems: Philips J. Res. **39** (1984) 1–94.
- 2) Y. Nishi, H.-H. Uchida and T. Honjyo: *Mater. Trans.* **45** (2004) 2902–2905.
- 3) Y. Nishi, H.-H. Uchida and T. Honjyo: *Mater. Trans.* **46** (2005) 126–129.
- 4) Y. Nishi, K. Numazaki and H.-H. Uchida: *Mater. Trans.* **48** (2007) 2964–2968.
- 5) Y. Nakamura, K. Sato, M. Kato, K. Oguro, and I. Uehara: Hydrogen Energy Processes, Ed. By T.N. Veziroglu *et al.*, (IAHE, vol. 11th, No. 2, 1996) 1287–1297.
- 6) B. Kim, N. Motai, H. Yabe, H.-H. Uchida and Y. Nishi: Proc. 6th Jpn.-Korea Joint Sympo. on Hydrogen Energy, (2001) pp. 189–194.
- 7) B. Kim, N. Motai, H. Yabe, H.-H. Uchida and Y. Nishi: *J. Adv. Sci.* **14** (2002) 15–16.
- 8) Y. Nishi, H.-H. Uchida, H. Yabe, B. Kim and T. Ogasawara: *J. Intelligent Materials and Structure* **17** (2006) 709–711.
- 9) Y. Nishi, T. Ogasawara and H.-H. Uchida: *Mater. Trans.* **48** (2007) 2715–2717.
- 10) Y. Nishi, J. Okawa, M. Kanda, A. Shimazu, R. Suenaga, Y. Ebihara, D. Kubo, H.-H. Uchida, K. Yuse and D. Guyomar: *Mater. Trans.* **50** (2009) 2460–2465.
- 11) J. Okawa, M. Kanda, K. Yuse, H.-H. Uchida, D. Guyomar and Y. Nishi: *Mater. Trans.* **51** (2010) 994–1001.
- 12) The Ceramic Society of Japan: *Handbook of Ceramics (2nd Edition)*, (Gihodo Shuppan, Tokyo, 2002) p.312.
- 13) H. Banse, G. Glauner-Breitinger, E. Hett, E. Hoffmann, K. Krohn, C. Linke-Schwelien, M. Mühling, A. Neuber and G. Pietsch-Wilcke : Gmelins Handbuch der Anorganischen Chemie System-Nummer 65 Palladium Lieferung 1, (Verlag Chemie GmbH, Weinheim, 1968) p.31.