巨形曲げ変形の可逆性動的モービルセメントコンポジット

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In order to generate the bending motion operated by pressure change in hydrogen gas, soft uni-morph composites were prepared, in which composites dispersed with not only driving particles of LaNi5 hydrogen storage alloy with Pd-Al2O3 catalyst powders to get high responsiveness, were piled up on a simple polyurethane sheet. Since the highest values of irreversible bending strain at the first hydrogenation cycles (ε2) under 0.3 MPa H2 gas and the maximum irreversible bending strain during hydrogenation cycles (ε2) were remarkably obtained at the 35 vol% of LaNi5 powders dispersed in polyurethane composites, the bending strain of reversible motion was detected from the first to the 8th hydrogenation (ε2) and ε3) under 0.2 MPa H2 gas. The bending strain of reversible motion of polyurethane composites sheet is more than 2000 ppm, which was approximately equal to that of silicone rubber composites and is extremely larger than that (300 ppm) of ABS resin composites. Responsiveness (de/dt) of cyclic motion of elastic deformed mover composites, which were constructed with 35 vol% LaNi5 dispersed powder and matrix of polyurethane or silicone rubber, were more than 10 times higher than that of ABS composite.

Keywords: hydrogen storage alloy, polyurethane, bending motion, mover composites, catalyst

1. Introduction

Hydrogen storage alloy, such as LaNi5, exhibits as large as 25% of volume expansion by hydrogenation under atmospheric pressure.1-3 In our previous works, two types of mover composites, which are LaNi5 film deposited on substrates2-5 and LaNi5 powders dispersed soft composites rod coated on silicone rubber,6-9 have been proposed. They exhibit the bending motion operated by hydrogen gas pressure change, as if a bi-metal operated by temperature change.

The soft mover composites are constructed with the driving rod coated on the supporting rod. The driving rod is a silicone rod with powders dispersion of LaNi5 hydrogen storage alloy, whereas the supporting rod is a pure silicone rubber.6-9 Since the motion responsiveness of the soft composites is, in general, not good, the strong improvement is required. It was also reported that the addition of catalyst of Pd-Al2O3 powders to the hydrogen storage alloy powders before dispersing improves the motion strain, as well as its responsiveness.10 Besides, the silicone rubber with good formability at room temperature exhibits the high limit strain of elasticity, whereas it is too soft.

To enhance the stiffness of mover composites rods with the good formability, the polyurethane prepared by solution casting (SC),1-3 is selected in the present paper. It exhibits the high elasticity, as well as high limit value of elastic strain. The influence of SC-treated polyurethane of both matrix and supporting rod in the composites on cyclic bending motion and its responsiveness has been investigated.

2. Experimental Procedure

2.1 Sample preparation

The sample LaNi5 alloys were pulverized by mortar under argon gas atmospheres, and then sieved to obtain a grain size of less than 100 μm in diameter. The chemical composition of hydrogen storage alloy powder was analyzed by energy dispersive X-ray spectroscopy (EDS: EMAX-5770, HORIBA) as LaNi5.2 Pd (5 mass%)-Al2O3 powders with 1 to 10 μm in diameter were mixed to the LaNi5 hydrogen storage alloy powders before dispersing in the polyurethane (PU) solution.11-13 A mover device in a uni-morph structure dispersed with powder hydrogen storage alloy was proposed. Two kinds of polyurethane sheets were prepared in order to construct a bi-metal structure. One of them was pure polyurethane (Estane Company, 58888 NAT 021) sheets. They are used supporting sheet. Another type was polyurethane dispersed with hydrogen storage alloy powders, mixed with Pd (5 mass%)-Al2O3 powders to enhance the responsiveness. They are used as driving sheets. These two kinds of films were prepared by a simple solution cast method. 1.8 g of polyurethane granules were dissolved in around 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 10 and 21 h for pure polyurethane and composite samples, respectively. 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, in order to eliminate residual solvent. Sample size was 40 mm × 10 mm × 1.0 mm (length × width × thickness). The variation of the thickness of film...
was 0.5 mm. All sheets were formed using a mold. The schematic diagram of mover composite sample was shown in the Fig. 1. The movements of the samples were observed under evacuation or introducing hydrogen, where the evacuation was carried out at 0.3 MPa within 5 s using a mechanical rotary pump. When the mass ratio of polyurethane (PU 1.8 g) and dimethyl holm amide (DMA 36 ml) is 1:2, the solution was prepared at 348 K in the mixer. The mixing period was 2 h at 4 cycle/s of rotation speed. The sample was solidified under air flow of fun to dry, when it was heated at 333 K for 10 and 21 h for polyurethane and LaNi$_5$ powders dispersed composites, respectively. The adhesion was performed for uni-morph composites after 20 h from start point of drying and just one hour before finish point of solidification. After solidification, it is cut out to the sample form.

2.2 Calculation of strain

The sample was activated in a glass-made drive evaluation apparatus under the hydrogen atmospheres of 0.3 MPa. From 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 ($\varepsilon$) of the actuator was calculated using eq. (1);

$$\varepsilon = \frac{\eta}{\rho}$$

where $\eta$ is a half thickness of the uni-morph soft composites and $\rho$ is a radius of curvature of the sheet center of actuator sample. The bending strain of motion $\varepsilon$ yields by the shape change before and after hydrogen gas absorption.

3. Results

3.1 Hydrogenation induced motion strain

Figure 2 shows the optical photographs of mover composites at the shape change by hydrogen gas supply under 0.3 MPa. When the composites were constructed with the supporting polyurethane sheet and the driving composites (polyurethane sheet) dispersed with both hydrogen storage alloy (35 vol%LaNi$_5$) and catalyze (Pd-Al$_2$O$_3$) powders. A bending motion of the composites is found under 0.3 MPa hydrogen gas pressure for $10^3$ s (see Fig. 2). This sample is bended from base point line to broken line after $10^3$ s. The soft composite sheet shows a tremendously large bending motion by hydrogenation because of volume expansion of the LaNi$_5$ powders in the driving sheet (right handed sheet in Fig. 2).

Figure 3 shows changes in bending strain of irreversible motion ($\varepsilon$) of composites distributed with each mixed ratio of LaNi$_5$ powders from 10 to 80 vol%LaNi$_5$ after exposure to hydrogen under 0.3 MPa against reaction time; $t$. The first hydrogenation for 3 h (more than 10000 s) tremendously induces the large motion strain from 2500, 3500, 1500 and 1500 ppm for composites dispersed with 10, 35, 50 and 80 vol%LaNi$_5$ powders in polyurethane (see Fig. 4), respectively.
The first evacuation cannot be perfectly reversed for all samples. Since the residual strain is found under evacuation, the cyclic operation of hydrogenation under 0.3 MPa H₂ gas pressure and evacuation is found as irreversible motion for all composites from 10 to 80 vol%LaNi₅ powders in polyurethane.

The second hydrogenation enhances the bending strain of the bending motion. Their yielding points start from 2500, 4000, 2000 and 1050 ppm for vol%LaNi₅ powders of 10, 35, 50 and 80, respectively. Besides, the second evacuation decreases the bending strain. It is led from the fact that the irreversible motions have shifted from the 1st to the 10th.

4. Discussion

4.1 Bending strain of irreversible motion of plastic deformed composites

Figure 4 shows changes in bending strain (ε) of irreversible motion, bending strain at the first hydrogenation under 0.3 MPa (ε₁), the maximum bending strain during irreversible motion cycles induced by hydrogenation under 0.3 MPa/evacuation (εm), recovered strain of irreversible motion just after the first hydrogenation (ε₁ r), and recovered strain of irreversible motion just after the 10th hydrogenation cycle (ε₁0 r) of mover composites against each mixed ratio of LaNi₅ powders from 10 to 80 vol%LaNi₅.

As shown in Figs. 3 and 4, recovered strain of irreversible motion just after the first hydrogenation (ε₁ r) is 400, 1100, 500, 800 ppm, and recovered strain of irreversible motion just after the 10th hydrogenation cycle (ε₁0 r) is 300, 350+/-50, 300 and 300 ppm for 10, 35, 50 and 80 vol%LaNi₅ powders dispersed composites, respectively. Furthermore, the maximum bending strain of irreversible motion is 2600, 5000, 3000 and 1700 ppm for composites dispersed with 10, 35, 50 and 80 vol%LaNi₅ powders dispersed in polyurethane.

The highest values of bending strains of irreversible motion of ε₁, εm, ε₁ r and ε₁0 r are found at 35 vol%LaNi₅ powders dispersed in polyurethane composites. The addition of hydrogen storage LaNi₅ alloy powders into polymer matrix expands the volume and increases the εm as well as ε₁. On the other hand, the elastic force induced by powders expansion mostly conducts the whole composites samples through the elastic deformed matrix, whereas it partially conducts them through the plastic deformed matrix with stress relaxation. Since decreasing the volume fraction of polymer matrix by the powder addition decreases the strain of elastic deformation of the composites materials, excess addition of the LaNi₅ powders decreases the εm as well as ε₁. Therefore, the maximum values of εm and ε₁ have been obtained at 35 vol%LaNi₅ in composites materials, as shown in Fig. 4.

Since the first hydrogenation tremendously deforms the polyurethane composites as indicated by ε₁ (see Fig. 3), it induces the plastic deformation, as well as the elastic deformation. Thus, the first evacuation process cannot be perfectly revered the strain. The residual strain just after evacuation is higher than that before the first hydrogenation. The residual plastic strain indicates (ε₁ r-ε₁) just before the second hydrogenation. The first hydrogenation shows not only high (ε₁0 r-ε₁) values, but also high ε₁ r values of deformed composites. Since the irreversible motion at the 10th cycle (ε₁0 r) is apparently smaller than that at the first hydrogenation (ε₁) under 0.3 MPa (see Fig. 4), the hydrogenation cycles roughly decrease the irreversible motion strain of all plastic deformed polyurethane composites (see Figs. 3 and 4). In addition, the ε₁0 r value doesn’t largely depend on composition dependence. Thus, it is possible that the ε₁0 r value, although it is not so large, is the saturated irreversible motion strain of the plastic deformed composites.

4.2 Giant bending strain of reversible motion within super-elastic deformation under 0.2 MPa

Although the hydrogenation induces the large plastic bending strain of mover composites with 35 vol%LaNi₅ powders dispersed in polyurethane, the reversible motion cannot obtain because of plastic deformation. When the hydrogenation is controlled in elastic deformation of matrix, the large strain of reversible motion is expected. Thus, the hydrogenation is performed under 0.2 MPa H₂ gas pressure.

Figure 5 shows the reversible motion of bending strain (ε) of mover composites (35 vol%LaNi₅ powders dispersed polyurethane, silicone rubber and ABS resin) against cyclic reaction time (t) under hydrogenation under 0.2 MPa/evacuation.

Although perfect reversible motion cannot be found for the ABS composites, the reversible motions were obtained for composites of both silicone rubber and polyurethane matrix. The hydrogenation enhances the bending strain at more than 2400 ppm for 20 s of hydrogenation time under 0.2 MPa H₂ gas. The evacuation for 20 s tremendously decreases the bending strain to zero. Since the residual strain is zero, this bending motion is reversible, that is, elastic deformation.

When the matrix exhibits the large plasticity limit of matrix, the large reversible motion strain would like to be obtained. Figure 6 shows the stress-strain curves of the elastic (a) and plastic (b) deformation for polyurethane, silicone rubber and ABS resin. Figure 7 exhibits changes in residual strain (εₜ) against the maximum bending strain...
Fig. 5 Reversible motion of bending strain ($\varepsilon$) of composites (35 vol%LaNi$_5$ powders dispersed polyurethane and silicone rubber) against cyclic reaction time ($t$) of hydrogenation 0.2 MPa/evacuation, together with bending motion strain of ABS composite.

Fig. 6 Bending stress-strain curves of elastic (a) and plastic (b) deformation for polyurethane (solid line), silicone rubber (broken line) and ABS resin (dotted line).

Fig. 7 Changes in residual strain ($\varepsilon_r$) against the maximum bending strain ($\varepsilon_{\text{max}}$) of stress-strain curves for polyurethane (solid line), silicone rubber (broken line) and ABS resin (dotted line). When the residual strain ($\varepsilon_r$) is zero, the biggest value of the maximum bending strain ($\varepsilon_{\text{max}}$) of stress-strain curves can be defined as the elasticity limit. The elasticity limit of polyurethane is 2.5 times larger than that of ABS resin, as well as slightly larger than that of silicon rubber. The large limit of reversible motion (see Fig. 5) corresponds to elasticity limits of stress-strain curves of matrix polymers (see Figs. 6 and 7).

4.3 Responsiveness ($de/dt$) of reversible and irreversible bending motion induced by hydrogenation

Figure 8 shows responsiveness ($de/dt$) of bending motion by hydrogenation of composites of 35 vol%LaNi$_5$ powders dispersed polyurethane (solid line) against reaction time ($t$). The perfectly fitting data of $de/dt$ can be obtained in the reversible elastic motion of 35 vol%LaNi$_5$ powders dispersed polyurethane from the first to the 8th cyclic reaction of hydrogenation under 0.2 MPa/evacuation. The reversible responsiveness ($de/dt$) generated by hydrogenation of the polyurethane composite is more than half of that of silicon rubber composites. Although the perfect reversible motion cannot be found for ABS composite under 0.2 MPa H$_2$ gas, the reversible hydrogenation responsiveness ($de/dt$) of the polyurethane composite is 10 times higher than that of ABS composites.

When the volume fraction of LaNi$_5$ powders is 35 vol%, in the composites, the responsiveness of bending motion of the composites is assumed to be dominated by the resistance to elastic deformation, that is, apparent hardening modulus (elasticity) of matrix polymers. Figure 6(a) shows bending stress-strain curves of elastic deformation for polyurethane, silicone rubber and ABS resin. As shown in Fig. 6, the apparent hardening modulus values are 0.3 MPa for silicone rubber, 3.5 MPa for ABS resin and 1.4 MPa for polyurethane, as well as 380–400 and 117 GPa of elasticity for Al$_2$O$_3$ and palladium, respectively. The apparent hardening modulus of polyurethane is smaller than that of ABS resin and higher than that of silicon rubber. Thus, the high responsiveness of both polyurethane and silicone rubber composites can be roughly explained by the low values of matrix elasticity (see Fig. 6(a)).
Responsiveness \((d\varepsilon/dt)\) of reversible motion (solid line in Fig. 8) is lower than that of irreversible motion (broken line) of the first hydrogenation, which is higher than that of reversible motion (solid line). This is because that the operating pressure of reversible motion (0.2 MPa) is lower than that of irreversible motion (0.3 MPa).

Responsiveness \((d\varepsilon/dt)\) of reversible elastic motion under 0.2 MPa \(\text{H}_2\) gas is generally higher than those of plastic deformed irreversible motion (broken lines) from the 2nd to the 8th hydrogenation under 0.3 MPa \(\text{H}_2\) gas pressure. The cyclic decay of responsiveness cannot be found of the elastic deformed reversible motion, whereas it decreases the responsiveness of the plastic deformed irreversible motion.

The hydrogenation expands the volume of the dispersed powders of hydrogen storage alloy. If the expansion generates the hardening induced by plastic deformation of polyurethane matrix, the cyclic decay can be explained. Therefore, when the expansion limit can be controlled under 0.2 MPa \(\text{H}_2\) gas pressure on hydrogenation, the reversible bending motion by hydrogenation of mover composite with 35 vol%LaNi\(_5\) powders dispersed in polyurethane can be obtained.

4.4 Recovered responsiveness \((d\varepsilon/dt)\) of bending motion induced by evacuation

Figure 9 shows recovered responsiveness \((d\varepsilon/dt)\) of bending motion by evacuation of mover composites of 35 vol%LaNi\(_5\) powders dispersed polyurethane hydrogenised under 0.2 and 0.3 MPa \(\text{H}_2\) gas pressure against reaction time \((t)\), together with motion of composites of 35 vol%LaNi\(_5\) powders dispersed silicone rubber and ABS resin under 0.2 MPa \(\text{H}_2\) gas pressure.

The perfectly fitting data of recovered \(d\varepsilon/dt\) can be also obtained in the elastic deformed reversible motion from the first to the 8th cycle for the polyurethane and silicon rubber composites by evacuation after hydrogenation at 0.2 MPa \(\text{H}_2\) gas pressure. Recovered responsiveness \((d\varepsilon/dt)\) by evacuation is also high for the polyurethane and silicon rubber composites, whereas the ABS composite also exhibits the low responsiveness of irreversible motion.

The recovered responsiveness \((d\varepsilon/dt)\) of reversible motion generated by evacuation after hydrogenation under 0.2 MPa \(\text{H}_2\) pressure of polyurethane composites is always higher than that of irreversible motion by evacuation after hydrogenation under 0.3 MPa \(\text{H}_2\). Although the cyclic motion decreases the responsiveness of the irreversible motion under 0.3 MPa \(\text{H}_2\), the decay of responsiveness of reversible motion cannot be found under 0.2 MPa \(\text{H}_2\). When the hydrogenation generates the hardening induced by plastic deformation of polyurethane matrix, the decay of recovered responsiveness of irreversible motion can be explained. Since the expansion limit can be controlled under 0.2 MPa \(\text{H}_2\) gas pressure on hydrogenation, the reversible motion by evacuation of mover composite with 35 vol%LaNi\(_5\) powders dispersed in polyurethane can be obtained.

5. Conclusion

In order to generate the bending motion operated by pressure change in hydrogen gas, soft uni-morph composites were prepared, in which polyurethane composites sheets, dispersed with not only driving particles of LaNi\(_5\) hydrogen storage alloy, but also Pd-Al\(_2\)O\(_3\) catalyst powders to obtain high responsiveness, was piled up on a simple polyurethane sheet.

(1) The highest values of irreversible bending strain at the first hydrogenation \((\varepsilon^1)\) under 0.3 MPa \(\text{H}_2\) gas and the maximum irreversible bending strain during hydrogenation cycles \((\varepsilon^m)\) were remarkably obtained at the 35 vol% of LaNi\(_5\) powders dispersed in polyurethane composites.

(2) The bending strain of reversible motion was detected from the first \((\varepsilon^1)\) to the 8th hydrogenation \((\varepsilon^8)\) under 0.2 MPa \(\text{H}_2\) gas. The reversible motions were obtained for composites of both silicone rubber and polyurethane matrix, whereas the perfect reversible motion cannot be found for the ABS composites.

(3) The maximum elastic bending strain of reversible motion of polyurethane composites sheet was found at more than 2000 ppm, which was approximately equal to that of silicone rubber composites. It was extremely larger than that of ABS resin composites (300 ppm).

(4) The perfectly fitting data of \(d\varepsilon/dt\) can be also obtained for the reversible motion from the first to the 8th cycle reaction of hydrogenation under 0.2 MPa \(\text{H}_2\) gas/evacuation for 35 vol%LaNi\(_5\) powders dispersed polyurethane.

(5) The reversible responsiveness \((d\varepsilon/dt)\) generated by hydrogenation of the polyurethane composite is more than half of that of silicone rubber composites. Although the perfect reversible motion cannot be found for ABS composite under 0.2 MPa \(\text{H}_2\) gas, the reversible hydrogenation responsiveness \((d\varepsilon/dt)\) of the polyurethane composite is 10 times higher than that of ABS composites.

(6) When the expansion limit can be controlled under 0.2 MPa \(\text{H}_2\) gas pressure on hydrogenation, the reversible
bending motion by hydrogenation of mover composite with 35 vol% LaNi$_5$ powders dispersed in polyurethane can be obtained.

(7) Although $ds/dt$ of irreversible motion of the first hydrogenation under 0.3 MPa H$_2$ pressure is higher than that of reversible motion under 0.2 MPa H$_2$ pressure, the responsiveness ($ds/dt$) of reversible motion is generally higher than that of irreversible motion.

(8) Recovered responsiveness ($ds/dt$) by evacuation after hydrogenation at 0.2 MPa H$_2$ gas pressure is also high for both polyurethane and silicon rubber composites, whereas the ABS composite exhibits the low recovered responsiveness.

(9) The recovered responsiveness ($ds/dt$) of reversible motion generated by evacuation after hydrogenation at 0.2 MPa H$_2$ gas pressure is always higher than that of plastic deformed irreversible motion by evacuation after hydrogenation at 0.3 MPa H$_2$ gas pressure.

Consequently, when the expansion limit can be controlled under 0.2 MPa H$_2$ gas pressure on hydrogenation, the reversible bending motion by hydrogenation of mover composite with 35 vol% LaNi$_5$ powders dispersed in polyurethane can be obtained.

Acknowledgement

Author would like to thank T. Ogasawara, K. Akazawa, A. Sato, T. Oikawa, B. Kim, Dr. H. Yabe, Dr. K. Iwata for their useful helps. This work is partially supported by INSA de Lyon and LGEF (CNRS) in France.

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