Effect of Aging Time on Shape Memory Properties of Sputtered Ni-rich Ni₂MnGa Alloy Films

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Ni₂MnGa alloy is an intelligent material with ferromagnetic and shape memory properties. The application of the alloy films to micro-actuators has been proposed. The Ni-rich Ni₂MnGa alloy films with a thickness of nearly 5 μm were deposited on Al₂O₃ substrates by a radio-frequency magnetron sputtering apparatus using a Ni₅₂Mn₂₄Ga₂₄ target. They were heat-treated at 1073 K for 36 ks for homogenization and ordering. The martensitic transformation temperatures of the heat-treated films were higher than room temperature. To investigate the effect of aging time on shape memory properties, the heat-treated films were aged at 673 K for various times between 0.9 and 57.6 ks in a constrained condition. The constraint-aged films showed the two-way shape memory effect by thermal cycling. Fine precipitates with a crystal structure of L1₂ were observed in the constraint-films aged for a long period. As for their two-way shape memory properties, a range of transformation temperature narrowed and the amount of macroscopic shape change increased with increasing aging time.

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1. Introduction

The ternary intermetallic compound Ni₂MnGa has ferromagnetic and martensitic transformation properties as first reported by Webster *et al.*¹⁾ It has the Heusler-type cubic crystal structure of L2₁ at high temperature and some martensitic crystal structures at low temperature.^{1–3)} The martensitic transformations occur in the ferromagnetic temperature region and can be controlled not only by temperature and stress but also by magnetic field.⁴⁾ However, the Ni–Mn–Ga bulk alloy is too brittle to be formed in a required shape. Furthermore, it has a disadvantage of very slow response to the shape memory effect.

To solve these problems, the use of the Ni–Mn–Ga alloy films prepared by the sputtering method has been proposed by the authors.^{5–8)} It may be applied for an actuator of micro-machines. The films with heat treatment at 1073 K showed high crystallinity and martensitic transformations.⁵⁾ When their use around room temperature is considered, martensitic transformations and the Curie temperature should be higher than room temperature. It was found that the heat-treated Ni-rich Ni₂MnGa alloy films met this requirement and showed the one-way shape memory effect.⁶⁾ Furthermore, the two-way shape memory effect (TWME) was found to be induced by the plastic deformation⁷⁾ and the constraint-aging method.⁸⁾ It is commonly accepted that the occurrence of the TWME has been ascribed to the relaxation of inhomogeneous stress fields in the parent phase by the formation of the preferentially oriented variants. The inhomogeneous stress fields will be generated for precipitates, a part of stress-induced martensitic phases and so on. In the present study, the occurrence of precipitates and the effect of aging time on the shape memory properties were investigated with respect to the heat-treated Ni-rich Ni₂MnGa alloy films prepared by the constraint-aging method.

2. Experimental Procedure

2.1 Preparation of films

Ni-rich Ni₂MnGa alloy films for studies on the TWME were deposited on Al₂O₃ substrates (thickness, 0.15 mm) by a radio-frequency (RF) magnetron sputtering apparatus using a Ni₅₂Mn₂₄Ga₂₄ target. The sputtering conditions were as follows: base pressure, $<2.5 \times 10^{-4}$ Pa; argon working-gas pressure, 6×10^{-1} Pa; substrate temperature, 323 K; sputtering power, 400 W. The thickness of the deposited films was attained at nearly 5 μm by controlling the sputtering time. These deposited films were heat-treated at 1073 K for 36 ks for homogenization and ordering, then, peeled from the Al₂O₃ substrates. Hereafter, these heat-treated films were called as 400 W–1073 K-films.

Some of the 400 W–1073 K-films with a flat shape were cut into 5 mm × 12 mm, deformed to a cylindrical shape, and then, fixed inside a silica tube whose inner diameter was 4 mm. Some of these constrained 400 W–1073 K-films were aged at 673 K for various times (t_{age}) between 0.9 and 57.6 ks in a flow of argon gas, then, rapidly cooled in air. One of the constrained 400 W–1073 K-films was aged at 673 K for 432 ks in a vacuum furnace, then, slowly cooled in it.

On the other hand, one of the 400 W–1073 K-films was fastened between flat Mo plates, aged at 673 K for 3.6 ks in a flow of argon gas, and then, rapidly cooled in air.

The other Ni-rich Ni₂MnGa alloy films with different properties (chemical composition, martensitic transformation temperatures, and so on) from the 400 W–1073 K-films were deposited at 50 W on poly-vinyl alcohol (PVA) substrates (thickness, 18 μm), which were soluble in hot water. These deposited films with a thickness of nearly 5 μm were separated from the PVA substrates, then, heat-treated at 873 K for 36 ks in a vacuum furnace. Hereafter, these heat-treated films were called as 50 W–873 K-films. The 50 W–873 K-films were prepared to study the crystal structure and mi-

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crostructure.

2.2 Characterization of prepared films

X-ray diffraction (XRD) studies for the heat-treated and aged 400 W–1073 K-films were made using Cu–K α radiation on an X-ray diffractometer (Rigaku, RAD-C) equipped with a heating stage in a temperature range from 303 to 373 K. The measurements were made while these films were held at

given temperatures in heating process. On the other hand, an XRD study for the 50 W–873 K-film was made with a conventional X-ray diffractometer (Rigaku, RINT2000) at room temperature. Transmission electron microscopy (TEM) studies and composition analyses were carried out using a transmission electron microscope (JEOL, JEM-3010) equipped with an energy dispersive X-ray spectrometer (EDS). Thin foils for the TEM examinations were prepared by twin jet electro-polishing in an electrolyte consisting of 20 vol% HNO₃–80 vol% CH₃OH.

The shape memory behavior of the constraint-aged 400 W–1073 K-films was observed using a digital video camera (Sony, DCR-PC100) in a temperature range from 300 to 330 K. Heating of these films was performed with a lump at $<0.04 \text{ K}\cdot\text{s}^{-1}$, and cooling at $<0.03 \text{ K}\cdot\text{s}^{-1}$.

3. Results and Discussion

3.1 Characteristics of heat-treated films

Chemical compositions, martensitic transformation temperatures and Curie temperatures of the heat-treated films were controlled by the sputtering power and heat-treatment conditions.⁵⁾ Their martensitic transformation temperatures increased with increasing nickel content, that is valence electron concentration (e/a). The valence electron configuration was assumed to be $3d^8 4s^2$ for Ni, $3d^5 4s^2$ for Mn and $4s^2 4p^1$ for Ga. These configurations are commonly used in electronic band calculations for the Heusler alloys.

The compositions of the 50 W–873 K-film and 400 W–1073 K-film were Ni–23.4 mol% Mn–23.0 mol% Ga ($e/a = 7.69$) and Ni–24.6 mol% Mn–21.7 mol% Ga ($e/a = 7.74$), respectively.⁶⁾ Although the martensitic transformation temperature of the 50 W–873 K-film was lower, that of the 400 W–1073 K-film was higher than room temperature. The reasons why they are rather different in spite of the fact that nickel content (that is e/a) of each film is similar to each other will be that the nickel content in the matrix and the degree of order

Fig. 1 XRD profiles of the 400 W–1073 K-film in a temperature range from 303 to 373 K. (a) shows the reversible martensitic transformation in heating process and (b) shows the existence of MnO phase.

Fig. 2 (a) selected area diffraction and (b) TEM dark field image using reflection spot A for the 400 W–1073 K-film at room temperature.

in the film are different.

Figures 1(a) and (b) show the XRD profiles of the 400 W–1073 K-film in a temperature range from 303 to 373 K. Figure 1(b) enlarged intensity of the diffraction patterns in Fig. 1(a) around 2θ of 41° . In Fig. 1(a), three diffraction peaks representing the martensitic phase clearly appear in a temperature range from 303 to 323 K and the (220) diffraction peak of the parent phase ($L2_1$ structure) from 333 to 373 K. In Fig. 1(b), the (200) peak of the MnO phase appears around 2θ of 40.6° at all temperature range. Figures 2(a) and (b) show the selected area diffraction and the TEM dark field image using the (200) reflection spot of the MnO phase exhibited in A circle, respectively, for the 400 W–1073 K-film at room temperature. In Fig. 2(b), it can be confirmed that the MnO particles with the sizes of about 10 nm homogeneously distributed

in the matrix. These results indicate that the MnO particles always exist in the heat-treated films.

Figures 3(a), (b) and (c) show the XRD profile, the selected area diffraction and the TEM dark field image using the reflection spot exhibited in B circle, respectively, for the 50 W–873 K-film at room temperature. In Figs. 3(a) and (b), in addition to diffraction peaks and reflection spots representing the parent and MnO phase, two peaks and spots representing the phase with the crystal structure of $L1_2$ appear, respectively. In Fig. 3(c), it is confirmed that the precipitates with the sizes of about 50–100 nm occur in this film. Also, it was found by the EDS analysis that the composition of the precipitates was Ni–14.7 mol%Mn–13.3 mol%Ga. Consequently, on the heat-treatment at comparatively low temperature, the precipitation of a compound with the approximate compositions of

Fig. 3 (a) XRD profile, (b) selected area diffraction and (c) TEM dark field image using reflection spot B for the 50 W–873 K-film at room temperature.

$\text{Ni}_3(\text{Mn}_{0.6}\text{Ga}_{0.4})$ with the crystal structure of L1_2 occurs in the films. On the precipitation of L1_2 , the nickel content in the matrix decreases, as a result, it is assumed that the martensitic transformation temperatures of this film decrease.

3.2 Characteristics of constraint-aged films

Figures 4(a) and (b) show the TEM bright field image and the selected area diffraction of the 400 W-1073 K-films constraint-aged at 673 K for 432 ks. The TEM observation

was made at room temperature. It was observed in Fig. 4(a) that the fine particles with the sizes of about 10 nm homogeneously distributed into this film. Also, in addition to the strong reflection spots of the martensite phase, the (200) spot of the MnO phase and (111) spot of L1_2 were seen in C and D circles, respectively. Figures 4(c) and (d) show the TEM dark field images taken using the reflection spots in the C and D circles, respectively. Although the number of the precipitates with the crystal structure of L1_2 is smaller than the

Fig. 4 (a) TEM bright field image, (b) selected area diffraction, (c) TEM dark field image using reflection spot C and (d) TEM dark field image using reflection spot D for the constraint-aged 400 W-1073 K-film ($t_{\text{age}} = 432.0$ ks) at room temperature.

Fig. 5 Effect of aging time on XRD profiles for the constraint-aged 400 W-1073 K-films at 373 K.

Fig. 6 Effect of aging method on XRD profiles for the aged 400 W-1073 K-films ($t_{\text{age}} = 3.6$ ks) at 373 K.

MnO phase, the fine precipitates homogeneously distributed into this film as seen in Figs. 3(c) and (d). Consequently, on constraint-aging at 673 K for 432 ks, the precipitation of L1₂ takes place in the 400 W–1073 K-film.

Figure 5 shows XRD profiles for the 400 W–1073 K-film constraint-aged at 673 K for 0.9 to 57.6 ks. The XRD measurements were made while the films were held at 373 K. In addition to the diffraction peaks representing the parent phase and the MnO phase, a very weak diffraction peak representing the precipitation of L1₂ appears slightly around 2θ of 43.3° in the profiles of the 400 W–1073 K-films constraint-aged for 3.6 and 57.6 ks. Furthermore, a weak diffraction peak appears around 2θ of 43° in the profiles of all the constraint-aged 400 W–1073 K-film samples. This diffraction peak becomes strong with increasing aging time.

Figure 6 shows XRD profiles for the 400 W–1073 K-films non-constraint-aged and constraint-aged at 673 K for 3.6 ks. The XRD measurements were made while the films were held at 373 K. Although a weak diffraction peak appears around 2θ of 43° in the profile of the constraint-aged 400 W–1073 K-film, it doesn't appear in the profile of the non-constraint-aged 400 W–1073 K-film. As a result of the XRD studies, it is considered that the phase corresponding to this peak may be a stress-induced martensitic one.

3.3 Effect of aging time on shape memory properties

The 400 W–1073 K-films after constraint-aging at 673 K for 0.9–57.6 ks were taken out of the silica tube and heated or cooled in a temperature range around the martensitic transformation temperatures. Figures 7(1) and (2) show the changes

Fig. 7 Effect of aging time on shape memory behavior for the constraint-aged 400 W–1073 K-films in the 2nd heating stage. (1) $t_{\text{age}} = 0.9$ ks and (2) $t_{\text{age}} = 57.6$ ks.

Fig. 8 Effect of aging time on temperature-strain curves for the constraint-aged 400 W–1073 K-films in the 2nd heating and cooling stages. (A)–(D) in (1) and (a)–(d) in (4) correspond to (A)–(D) in Fig. 7(2) and (a)–(d) in Fig. 7(1), respectively.

in the shape of 400 W–1073 K-films constraint-aged for 0.9 and 57.6 ks, respectively, in the 2nd heating. Figure 8 shows the temperature-strain curves obtained from the shape change in the 2nd thermal cycling. The strain at the outer surface was given by $\varepsilon = (d_s/2)/r_T$, where d_s is the thickness of films and r_T is the radius of a curvature for the bent films at each temperature. It is clear that the constraint-aged 400 W–1073 K-films show the TWME. The width of thermal hysteresis, which decreases with increasing aging time, is about 2 K when the aging time is 57.6 ks. Also, the reversible strain increases with increasing aging time. Furthermore, the temperatures of the shape change increase with increasing aging time up to 14.4 ks, then, they decrease with increasing aging time. These results suggest that both of the stress-induced martensitic phase and the precipitates exist as the inhomogeneous stress fields in the constraint-aged 400 W–1073 K-films.

When the aging time is short, the stress-induced martensitic phase is considered to be mainly responsible for the TWME of the constraint-aged 400 W–1073 K-films. Also, the precipitates are considered to be responsible for it with increasing aging time. The MnO particles may have no effect on the TWME because they always exist in the 400 W–1073 K-films. A further study is needed to clarify its mechanism.

4. Summary

Ni-rich Ni_2MnGa films were deposited on an Al_2O_3 substrate with a RF magnetron sputtering apparatus using a $\text{Ni}_{52}\text{Mn}_{24}\text{Ga}_{24}$ target. The occurrence of precipitates and the effect of aging time on shape memory properties were investigated at various constraint-aging method.

The obtained results are summarized as follows:

- (1) The fine precipitates with crystal structure of L_{12} occurred in the constraint-aged 400 W–1073 K-films by aging for a long period.
- (2) The thermal hysteresis on the TWME of the constraint-aged 400 W–1073 K-films decreases with increasing aging time.
- (3) The reversible strain on the TWME of constraint-aged 400 W–1073 K-films increases with increasing aging time.

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