

Magnetic-field Controlled Two-way Shape Memory Effect of Ni₂MnGa Sputtered Films

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Shape memory effect by magnetic field is interesting and important for physics and application. The sputtered films of Ni₂MnGa were prepared by a radio-frequency magnetron sputtering apparatus using Ni_{52.5}Mn₂₂Ga_{25.5} target. The obtained films were heat-treated at 1073 K for homogenization and atomic ordering, and then cooled in a furnace. They were constrained in a silica tube and heated to make the two-way shape memory alloys. The two-way shape memory effect by heating and cooling was confirmed. The film was set into a chamber in which temperature was controlled. Magnetic field was applied parallel to the film surface up to 5 T using a super-conductor magnet. The radius of curvature in the film decreased with increasing magnetic field and increased with decreasing magnetic field. The shape change of film under magnetic field was recorded by a video camera. The strain in the film increased with increasing magnetic field and decreased with decreasing magnetic field. The experiments were performed at constant temperature between A_s^* and A_f^* , and M_s^* and M_f^* . These phenomena show the two-way shape memory effect.

Key words: two-way shape memory effect, sputtered film, ferromagnetic shape memory alloy, martensitic transformation, constraint-aging

1. INTRODUCTION

The ternary Ni₂MnGa alloy has a ferromagnetic property and a shape memory effect. It has the Heusler type crystal structure at high temperature and some martensitic crystal structures at low temperature [1-3]. The martensitic transformation of stoichiometric composition Ni₂MnGa occurs in the ferromagnetic region below Curie temperature 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 by temperature change.

To solve these problems, the use of the Ni-Mn-Ga alloy films prepared by the sputtering method has been proposed by the authors [5-7]. It may be applied for an actuator of micro-machines. In order to use this actuator at around room temperature, martensitic transformation 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. Martensitic transformation temperature increased and Curie temperature slightly decreased with increasing nickel content of the composition of Ni_{2+x}Mn_{1-x}Ga ($x=0\sim 0.19$) [8]. The chemical composition of film depends on that of target and sputtering electric power [5]. Two-way shape memory effect by heating and cooling was found to be induced by the plastic deformation [6] and the constraint-aging method [7]. However, the shape memory effect of this Ni₂MnGa sputtered film by magnetic field has not been studied.

In the present study, the two-way shape memory effect by magnetic field has been investigated using Ni-rich Ni₂MnGa alloy films prepared by the constraint-aging method.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of films

The Ni-rich Ni₂MnGa films were deposited on a poly-vinyl alcohol (PVA) substrate with a radio-frequency (RF) magnetron sputtering apparatus (Shibaura, CFS-4ES) using a Ni_{52.5}Mn₂₂Ga_{25.5} 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, 50 W. The thickness of the deposited films was about 5 μ m by controlling the sputtering time. After deposit, the films were separated from the PVA substrate by using hot water and then films were heat-treated at 1073 K for 36 ks for homogenization and atomic ordering.

After heat-treatment, the films were cut into 5 mm \times 12 mm, deformed to a cylindrical shape, and then, fixed inside a silica tube whose inner diameter was 4 mm. These constraint films were aged at 673 K for 14.4 and 57.6 ks in a flow of argon gas, then, rapidly cooled in air. The composition of the films was determined by an inductively coupled plasma (ICP) spectrometry (Seiko, SPS-1200A). The composition of film was Ni_{56.0}Mn_{22.2}Ga_{21.8}.

2.2 Measurements of shape memory effect

The constraint-aged film was set into a chamber in which temperature was controlled. The shape memory behavior of the films was observed using a digital video camera (Sony, DCR-PC120). The measurement was performed from 295 to 383 K.

Magnetic field was applied parallel to film surface up to 5 T using a super-conductor magnet (Sumitomo heavy industries, HF%-100VT-50HT) at various temperatures.

Strain was calculated from the curvature of film at various temperatures and magnetic fields.

3. RESULTS AND DISCUSSION

3.1 Shape memory effect by thermal change

Fig. 1 shows the photographs of shape change of Ni_{56.0}Mn_{22.2}Ga_{21.8} film constrained at 673 K for 57.6 ks during heating and cooling. An end of the film was fixed and another end was free. The curvature of film increased with increasing temperature from 315 to 383 K, then it decreased with decreasing temperature from 383 to 315 K. Heating and cooling rate was 3.3×10^{-2} K/s. Temperatures in the chamber were monitored at several points and temperature distribution was almost constant. This shape change is two-way shape memory behavior. The film constrained at 673 K for 14.4 ks showed the similar behavior during heating and cooling. In this case, shape change was observed from 295 to 371 K. The measurement was performed in a temperature range of martensitic and reverse martensitic transformation. From this observation, strain ε ($= (d_s/2) / r_T$, d_s : thickness of film, r_T : radius of curvature), accompanied with the shape memory effect of the Ni_{56.0}Mn_{22.2}Ga_{21.8} films constrained at 673 K for 14.4 and 57.6 ks, respectively, was shown in Fig. 2. Heating process, (a)-(d), and cooling process, (e)-(h) are shown in Figs. 1 and 2.

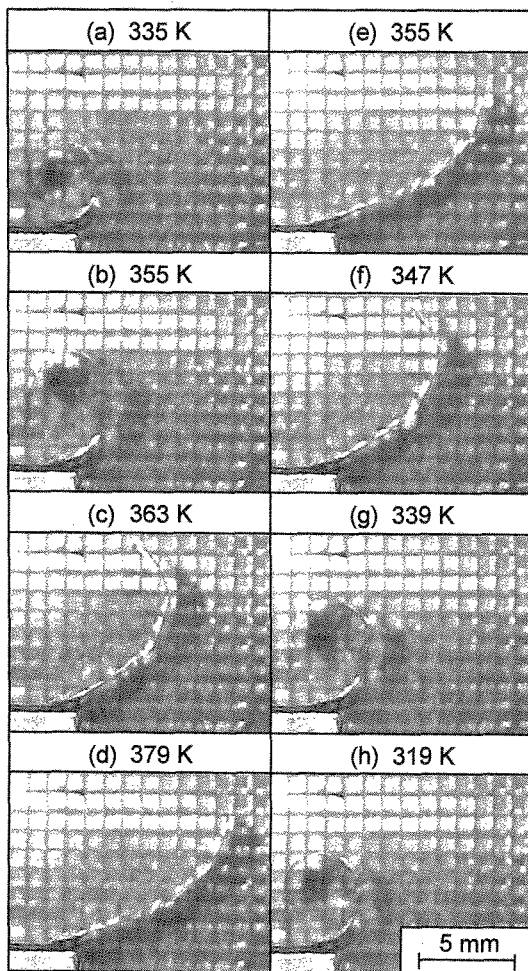


Fig. 1 Two way shape memory behavior of the Ni_{56.0}Mn_{22.2}Ga_{21.8} film constrained at 673 K for 57.6 ks. (a)-(d): heating. (e)-(h): cooling.

Strain vs. temperature curves present a similar behavior during heating and cooling. The amount of strain accompanied with the shape change was different from each other in constrained time for 14.4 and 57.6 ks. Strain was constant in the low and high temperature region in (A) and (B) in this figure. The difference of strain between strain at low temperature and that at high temperature was large in the case of aging time of 57.6 ks compared to that in aging time of 14.4 ks.

Temperatures, A_s^* , A_f^* , M_s^* and M_f^* , were defined as the inflection points obtained by the interpolated method. During heating, the strain in the low temperature region decreased and changed in the high temperature region. Corresponding to A_s , reverse martensitic transformation start temperature, A_s^* was defined. A_f^* , M_s^* and M_f^* were defined in the similar meaning. The temperatures, A_s^* , A_f^* , M_s^* and M_f^* , the strain at low temperature, ε_{LT} , strain at high temperature, ε_{HT} , two way shape memory effect strain, ε_{TWME} , and the temperature hysteresis were listed in Table 1. ε_{TWME} is the difference between ε_{HT} and ε_{LT} . The cooling gradient, $\alpha_{cooling}$, and the heating gradient, $\alpha_{heating}$, were calculated as listed in this table. These gradients were defined as a ratio of the strain and the difference in transformation temperature, $\alpha_{cooling} = \varepsilon_{TWME} / (A_f^* - A_s^*)$ and $\alpha_{heating} = \varepsilon_{TWME} / (M_s^* - M_f^*)$. They indicate the magnitude of strain accompanied by the martensitic and reverse martensitic transformations per temperature change of 1 K. The value in the case of aging time, t_{age} , of 57.6 ks was twice of that in aging time, t_{age} , of 14.4 ks. Effective two-way shape memory strain can be realized in the aging time of 57.6 ks.

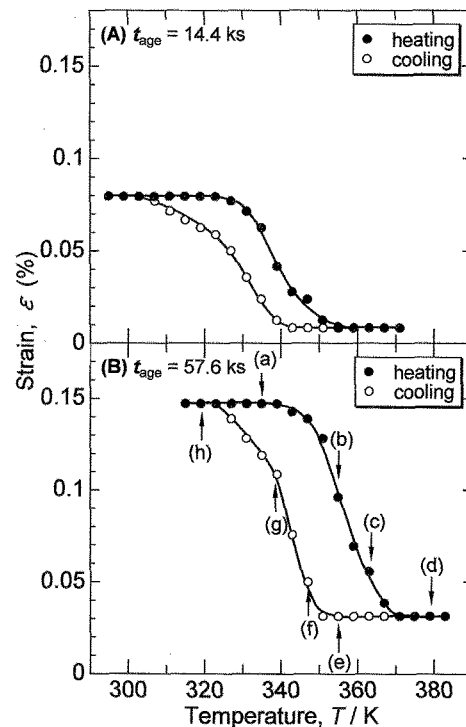


Fig. 2 Strain accompanied with two way shape memory effect of Ni_{56.0}Mn_{22.2}Ga_{21.8} films constrained at 673 K. Constraint-aging times, t_{age} , are 14.4 ks (A) and 57.6 ks (B), respectively.

Table 1 Aging time, martensitic transformation temperatures, strain of TWME, gradient and hysteresis of the films.

$t_{\text{age}} / \text{ks}$	M_s^* / K	M_f^* / K	A_s^* / K	A_f^* / K	$\varepsilon_{\text{TWME}}$	α_{cooling}	α_{heating}	hysteresis / K
14.4	339	319	331	349	0.071	3.6×10^{-3}	3.6×10^{-3}	10
57.6	349	335	349	363	0.116	8.3×10^{-4}	8.3×10^{-4}	14

3.2 Shape memory effect by magnetic field change

The shape change under the magnetic field up to 5 T was observed. Observation of the shape change and analysis of the strain were performed by the same method as in the case of shape memory effect by temperature change.

Fig. 3 shows strain vs. magnetic field curves of the $\text{Ni}_{56.0}\text{Mn}_{22.2}\text{Ga}_{21.8}$ film constrained at 673 K for 14.4 ks at temperature between A_s^* and A_f^* , and M_s^* and M_f^* , respectively. The strain at 345 K between A_s^* and A_f^* increased and decreased slightly with increasing and decreasing magnetic field. The strain before the applied magnetic field was same as that after the applied magnetic field. The strain at 335 K between M_s^* and M_f^* increased slightly with increasing magnetic field up to 2 T and then it increased largely up to 5 T. With decreasing magnetic field from 5 T, the strain decreased monotonously. At 0 T, the strain did not recover perfectly.

Fig. 4 shows strain vs. magnetic field curves of the $\text{Ni}_{56.0}\text{Mn}_{22.2}\text{Ga}_{21.8}$ film constrained at 673 K for 57.6 ks at temperature between A_s^* and A_f^* , and M_s^* and M_f^* , respectively. The behavior in the effect of magnetic field on the strain was similar as that in aging time of 14.4 ks. The change of strain at 355 K between A_s^* and A_f^* and in 347 K between M_s^* and M_f^* was larger than that of

aging time of 14.4 ks.

The change of strain by the magnetic field up to 5 T between A_s^* and A_f^* was very small. It can be considered that the martensitic transformation induced by the magnetic field did not occur because measurement temperature was higher than M_s^* .

After the applied magnetic field, the strain did not recover. Large driving force is necessary in order to transform from the induced martensite phase by the magnetic field to the original phase.

In the measurement at the temperature between M_s^* and M_f^* , the strain change induced by the magnetic field up to 5 T corresponds to that obtained by cooling of 4 degree.

ε_{0T} and ε_{5T} are defined as the strain before and after the application of magnetic field up to 5 T. $\Delta\varepsilon_B$ is the difference between ε_{0T} and ε_{5T} , as follows.

$$\Delta\varepsilon_B = \varepsilon_{5T} - \varepsilon_{0T} \quad (1)$$

ΔT_B is defined as the temperature change required for the shape memory effect by thermal change, in order to obtain the same strain change ($\Delta\varepsilon_B$) which is observed by the magnetic field.

$$\Delta T_B = \varepsilon_B / \alpha \quad (2)$$

Large strain change will be obtained by a small

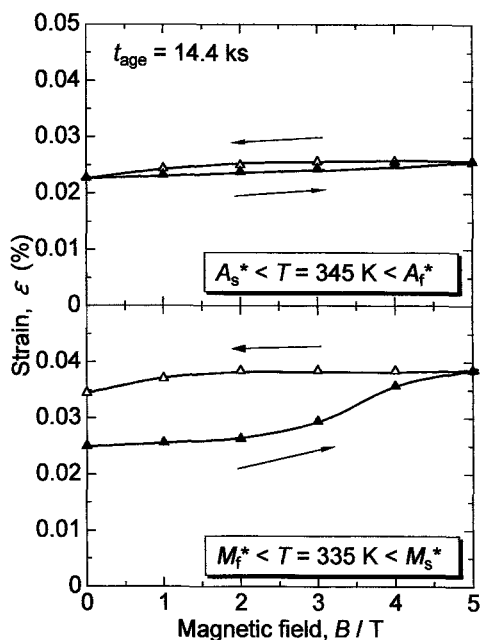


Fig. 3 Strain vs. magnetic field curves of the $\text{Ni}_{56.0}\text{Mn}_{22.2}\text{Ga}_{21.8}$ films constrained at 673 K for 14.4 ks at temperature between A_s^* and A_f^* , and M_s^* and M_f^* , respectively.

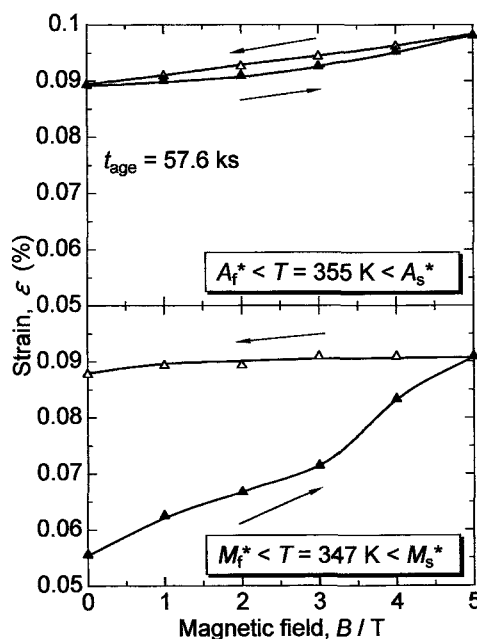


Fig. 4 Strain vs. magnetic field curves of the $\text{Ni}_{56.0}\text{Mn}_{22.2}\text{Ga}_{21.8}$ film constrained at 673 K for 57.6 ks at temperature between A_s^* and A_f^* , and M_s^* and M_f^* , respectively.

Table 2 Strain and temperature at each constrained aging time.

$t_{\text{age}} / \text{ks}$	$\frac{\Delta\varepsilon_{\text{B}}}{(M_{\text{s}}^* \sim M_{\text{f}}^*)}$	$\frac{\Delta\varepsilon_{\text{B}}}{(A_{\text{s}}^* \sim A_{\text{f}}^*)}$	$\frac{\Delta T_{\text{B}} / \text{K}}{(M_{\text{s}}^* \sim M_{\text{f}}^*)}$	$\frac{\Delta T_{\text{B}} / \text{K}}{(A_{\text{s}}^* \sim A_{\text{f}}^*)}$
14.4	1.4×10^{-2}	2.9×10^{-3}	3.9	0.8
57.6	3.5×10^{-2}	8.8×10^{-3}	4.2	1.1

magnetic field in the case of large ΔT_{B} .

Table 2 shows the values of $\Delta\varepsilon_{\text{B}}$ and ΔT_{B} at each constrained temperature.

4. SUMMARY

Ni_{56.0}Mn_{22.2}Ga_{21.8} sputtered films were prepared by a RF magnetron sputtering apparatus. These films aged under constrain showed a two-way shape memory effect by thermal change as well as magnetic field.

The strain by the magnetic field is different from each other at the measurement temperature.

In the measurement at the temperature between M_{s}^* and M_{f}^* , the strain change induced by the magnetic field up to 5 T corresponded to that obtained by cooling of 4 degree.

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References

- [1] P. J. Webster, K. R. A. Ziebeck, S. L. Town and M. S. Peak, *Philos. Mag. B*, **49**, 295-310 (1984).
- [2] J. Pons, V. A. Chernenko, R. Santamarta and E. Cesari, *Acta Mater.*, **48**, 3027-3038 (2000).
- [3] B. Wedel, M. Suzuki, Y. Murakami, C. Wedel, T. Suzuki, D. Shindo and K. Itagaki, *J. Alloys Comp.*, **290**, 137-143 (1999).
- [4] K. Ullakko, *J. Mater. Eng. Perform.*, **5**, 405-409 (1996).
- [5] K. Ohi, S. Isokawa, M. Ohtsuka, M. Matsumoto and K. Itagaki, *Trans. Mater. Res. Soc. Japan*, **26**, 291-294 (2001).
- [6] M. Ohtsuka, M. Matsumoto and K. Itagaki, *Trans. Mater. Res. Soc. Japan*, **26**, 201-204 (2001).
- [7] S. Isokawa, M. Suzuki, M. Ohtsuka, M. Matsumoto and K. Itagaki, *Mater. Trans.*, **42**, 1886-1889 (2001).
- [8] M. Matsumoto, T. Takagi, J. Tani, T. Kanomata, N. Muramatsu and A. N. Vasil'ev, *Mater. Sci. Eng.*, **A 273-275**, 326-328 (1999)

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