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Two-way Shape Memory Behavior of Ni_2MnGa Sputtered Films

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The ternary intermetallic compound Ni_2MnGa is an intelligent material, which has both a ferromagnetic property and a shape memory effect (SME). Use of shape memory alloy films for an actuator of micro-machines is very attractive because of its large recovery force and response to magnetic field. The purpose of the present study is to clarify the relationships between the shape memory behavior and fabrication conditions of the Ni_2MnGa films. The Ni_2MnGa films with a thickness of nearly 5 μm were deposited with a radio-frequency magnetron sputtering apparatus using a $Ni_{50}Mn_{25}Ga_{25}$ or $Ni_{52}Mn_{24}Ga_{24}$ target. They were heat-treated at 1073 K for homogenization and ordering, and then cooled in a furnace. The composition of the films depended on the sputtering power. The martensitic transformation temperature of the heat-treated films increased with increasing nickel content. The effect of plastic deformation and constraint aging on SME was investigated. After plastic deformation, the two-way SME was shown through the martensitic transformation and its reversion. The X-ray diffraction peaks from stress-induced martensitic phase was found. The constraint-aged films also showed the two-way SME not only by thermal cycling but also on an application of magnetic field.

Key words: Nickel-manganese-gallium, Sputter-deposition, Martensitic transformation, shape memory effect, constraint-aging

1. INTRODUCTION

The ternary intermetallic compound Ni_2MnGa is an intelligent material, which has both a ferromagnetic property and a shape memory effect (SME). The martensitic transformation can be controlled not only by temperature and stress but also by magnetic field [1]. It has the Heusler-type cubic crystal structure of $L2_1$ at high temperature and some martensitic crystal structures at low temperature [2-4]. The martensitic transformation occurs within the ferromagnetic region. This allows controlling its shape by an external magnetic field. If the SME appears under magnetic field, its response will be faster than that of thermal one.

As it is widely admitted, use of shape memory alloy films for an actuator of micro-machines is very attractive because of its large recovery force and response to magnetic field. Ni_2MnGa alloy is one of promising shape memory materials for an actuator with smart properties. However, the Ni_2MnGa bulk alloy is too brittle to be formed in a required shape. Furthermore, it has a disadvantage of very slow response to the SME.

To solve this problem, use of the Ni_2MnGa films prepared by a sputtering method has been proposed by the authors [5-8].

It is considered that the differences in sputtering conditions, such as composition of the target, sputtering power and substrate temperature, give significant effects on the characteristics of the films. The authors reported that the Ni_2MnGa sputtered films with heat treatment at 1073 K showed high crystallinity, martensitic transformations [5] and one-way SME [7]. Nevertheless, the effect of fabrication conditions on the two-way SME of these films has not been investigated systematically. Hence, the purpose of the present study is to investigate the effects of plastic deformation and constraint aging on SME controlled not only by temperature but also by magnetic field.

2. EXPERIMENTAL PROCEDURE

The Ni_2MnGa films were deposited on a poly-vinyl alcohol (PVA) substrate (thickness: 18 μm), which was soluble in hot water, or alumina one (thickness: 150 μm) with a radio-frequency (RF) magnetron sputtering apparatus (Shibaura, CFS-4ES) using two kinds of Ni-Mn-Ga targets whose nominal compositions were $Ni_{50}Mn_{25}Ga_{25}$ and $Ni_{52}Mn_{24}Ga_{24}$. These targets had stoichiometric Ni_2MnGa composition and higher nickel content than the stoichiometric one, respectively.

The sputtering conditions were as follows. The sputtering power (W_S) was 50 and 400 W. The substrate temperature was kept at 323 K by cooling water. The atmosphere used for the discharge was high purity argon (> 99.9995 %Ar) at a flow rate of 230 mm^3s^{-1}. The thickness of deposited films was attained at nearly 5 μm, which was measured by controlling the sputtering times.

The films deposited at 50 W on the PVA substrate using a $Ni_{50}Mn_{25}Ga_{25}$ target were separated from the substrate and fastened between straight Al_2O_3 plates (thickness: 2.5 mm). The separated films were annealed at 1073 K for 3.6 ks under vacuum condition of 2 × 10^{-4} Pa and then slowly cooled down in the furnace for homogenization and ordering.

On the other hand, the films deposited at 400 W on the alumina substrate using a $Ni_{52}Mn_{24}Ga_{24}$ target were annealed at 1073 K for 36 ks in a vacuum furnace under 2×10^{-4} Pa and then slowly cooled down in the furnace. After that, they were mechanically separated from the substrate. These homogenized films, which had a straight shape, were cut into 5 mm × 10 mm and deformed to a cylindrical shape. The deformed films were fixed inside a silica tube whose inner diameter was 4 mm. The constraint films were aged at 573 - 773 K for 0.9 - 57.6 ks in a flow of argon gas, and then rapidly cooled.

The two-way SME of the plastic-deformed and constraint-aged films was investigated using a digital video camera (Sony, DCR-PC100) in a temperature range of 297 - 345 K. The films were heated with a lamp. Furthermore, the influence of a magnetic field on the two-way SME of constraint-aged film was investigated. Magnetic field was applied parallel to the film surface up to 10 T using a super-conductor magnet.

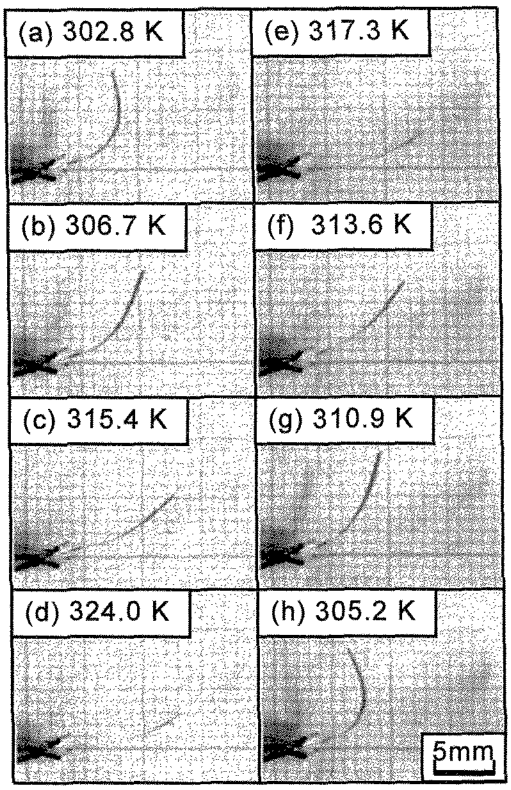

Fig. 1 Two-way shape memory effect of the plastic-deformed Ni_2MnGa film by heating ((a)-(d)) and cooling ((e)-(h)).

3. RESULTS AND DISCUSSION

3.1 Characteristics of heat-treated films

The change in composition, martensitic transformation temperature and Curie temperature of the heat-treated films with the sputtering power has been reported [6, 7].

Two different compositions of Ni_2MnGa films were used in the present study. The composition, martensitic transformation temperature and Curie temperature for the heat-treated films, which were sputtered at 50 W using a $Ni_{50}Mn_{25}Ga_{25}$ target and at 400 W using a $Ni_{52}Mn_{24}Ga_{24}$ target, are summarized in **Table 1**.

3.2 Two-way SME of plastic-deformed film

The SME of the plastic-deformed films was investigated. **Figure 1** shows typical spontaneous shape change during heating and cooling for the plastic-deformed film [8]. The film was sputtered at 50 W using the $Ni_{50}Mn_{25}Ga_{25}$ target after the heat treatment at 1073 K. The heat- treated film, which has a straight shape, was bent at room temperature and then heated up to 335 K. The bent film changes its shape toward the original straight one during heating (Fig. 1 (a-d)). However, the shape does not recover to the original one even after heating up to 335 K. In the next cooling step, the film bends automatically (Fig. 1 (e - h)).

Figure 2 shows a plot of the spontaneous shape change against the observation temperature [8]. Each shape change is expressed by the radius of curvature for

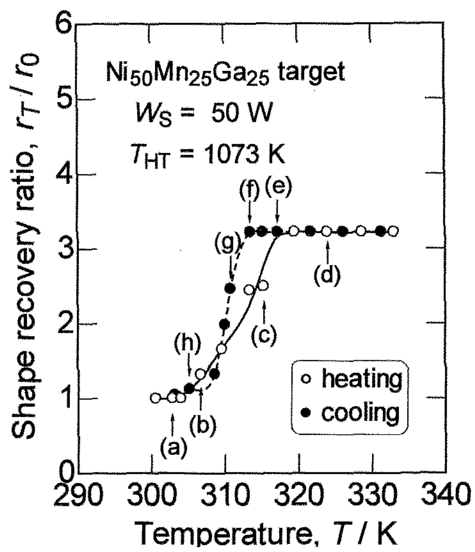

Fig. 2 Temperature dependence of shape change for the plastic-deformed Ni_2MnGa film by heating and cooling. The shape recovery ratio, r_T/r_0, is obtained from Fig. 1.

Table 1 Composition, martensitic transformation temperature and Curie temperature of the heat-treated films.

Composition	Condition	M_s / K	M_f / K	A_s / K	A_f / K	T_C / K
Ni - 25.3 mol% Mn - 22.8 mol% Ga	$Ni_{50}Mn_{25}Ga_{25}$ target W_S: 50 W Heat treat.: 1073 K - 3.6 ks	290	281	294	301	347
Ni - 23.4 mol% Mn - 23.0 mol% Ga	$Ni_{52}Mn_{24}Ga_{24}$ target W_S: 400 W Heat treat.: 1073 K - 36 ks	315	311	316	321	345

a bent film at each temperature (r_T) normalized by the initial radius of curvature (r_0) and they are obtained from Fig. 1. The temperature hysteresis of the shape change is small. It was recognized that the shape recovery change started from 304 K and continued up to 318 K by heating. These temperatures were higher than the reverse martensitic transformation start and finish temperatures (A_s, A_f) shown in Table 1.

The XRD pattern of this heat-treated film shows the Heusler-type cubic structure at RT [7]. After bending deformation, the intensity of diffraction peaks from the parent phase decreased and the diffraction peaks from the martensitic one was also observed [8]. The stress-induced martensitic phase always exists at RT in the film with two-way SME. It is considered that the transformation temperatures of the heat-treated film become higher after bending deformation. In this way, it is clarified that the plastic-deformed film shows the two-way SME by heating and cooling.

3.3 Two-way SME of constraint-aged film

For the SME of the constraint-aged film, the spontaneous shape change in the 1st heating ((a) - (d)), 1st cooling ((e) - (f)) and 2nd heating ((g) - (h)) are shown in **Figure 3** [9]. The film after constraint-aging at 673 K for 1.8 ks was taken out of the silica tube and heated and cooled in temperature ranges around martensitic transformation temperatures.

A temperature - strain curve was obtained from the spontaneous shape change and is shown in **Figure 4** [9]. The strain of outer surface was given by $\varepsilon = (d_S / 2) / r_T$, where d_S is the thickness of the film and r_T is the radius of a curvature for the bent film at each temperature. The points (a) - (h) in Fig. 4 correspond to those in Fig. 3. In the first heating, the cylindrically bent film changes the shape toward the original straight one before the constraint-aging. After heating up to 333 K, it does not recover to the original one. In the next cooling step, the film automatically starts bending (Fig. 3 (d) - (f)). It is clear from these observations that the film prepared with the constraint-aging method shows the two-way SME by thermal cycling.

3.4 Effect of constrain-aging condition on SME

The films were constraint-aged for 1.8 ks at 573, 673 and 773 K and the temperature - strain curves in the 2nd thermal cycling are shown in **Figure 5**. It is shown that, for 1.8 ks, the temperature of shape change decreases while the reversible strain increases with increasing aging temperature. It is noteworthy in this case that the thermal hysteresis remarkably decreases with increasing aging temperature. The width decreases from about 2.5 to 0 K when the aging temperature is changed from 573 to 773 K. On the other hand, those for the films constraint-aged at 673 K for 0.9, 3.6, 14.4 and 57.6 ks are shown in **Figure 6**. The width of thermal hysteresis, which decreases with increasing aging time, is about 0 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. Both the stress-induced martensitic phase and the Ni_3(Mn, Ga) precipitates existed in the constraint-aged films [10].

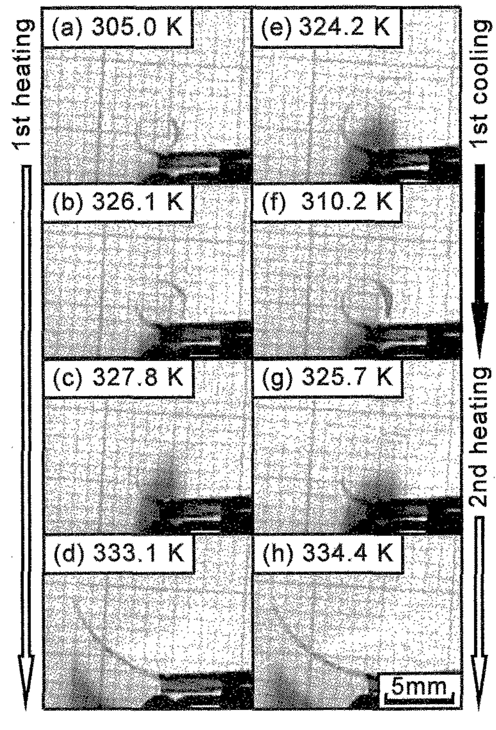

Fig. 3 Two-way shape memory effect of the film constraint-aged at 673 K for 1.8 ks in the 1st heating ((a) - (d)), 1st cooling ((e) - (f)) and 2nd heating ((g) - (h)).

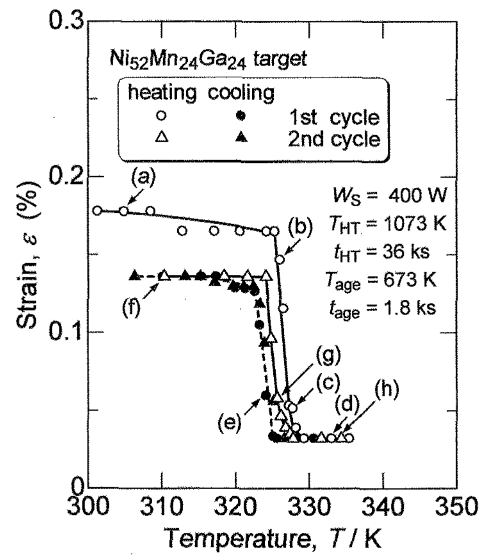

Fig. 4 Temperature - strain curve for the film constraint-aged at 673 K for 1.8 ks.

When the aging time is short, the stress-induced martensitic phase is considered to be mainly responsible for the two-way SME of the constraint-aged films. Also, the precipitates are considered to be responsible for it with increasing aging time.

3.5 Magnetic induced SME of constrain-aged film

The influence of a magnetic field on the two-way SME of the constraint-aged film was investigated. **Figure 7** shows the strain of the film constraint-aged at

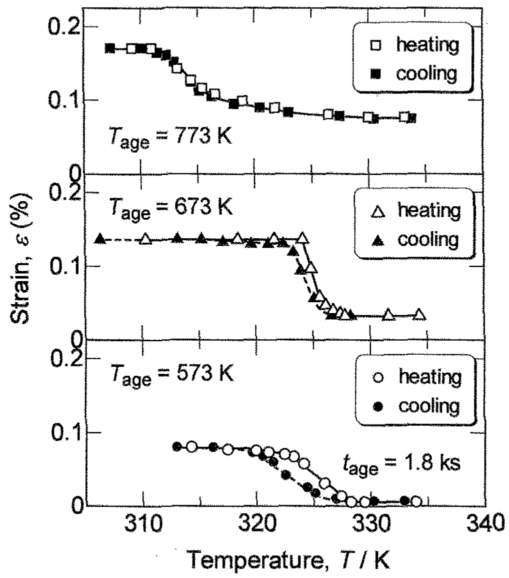

Fig. 5 Effect of aging temperature on temperature - strain curves for the constraint-aged films in the 2nd thermal cycling (t_{age} = 1.8 ks).

673 K for 3.6 ks against magnetic field. The film was heated up to just above the A_f temperature. The strain of the film increases with increasing magnetic field and decreases decreasing magnetic field. These phenomena show the two-way SME controlled by magnetic field.

4. SUMMARY

The results obtained in the present study are summarized as follows:

(1) The plastic-deformed film shows a two-way SME by heating and cooling. The constraint-aged film also shows a two-way SME by thermal cycling.

(2) The width of thermal hysteresis decreases with increasing aging temperature and aging time. The reversible strain increases with increasing aging time and aging temperature up to 673 K.

(3) The constraint-aged film shows a two-way SME by magnetic field.

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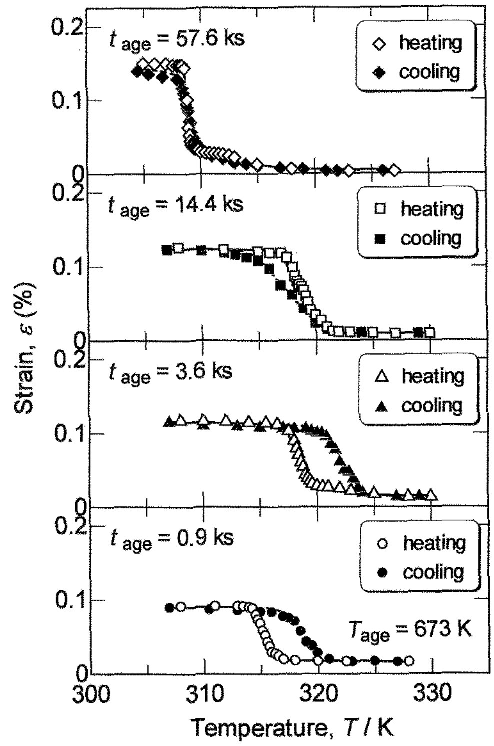

Fig. 6 Effect of aging time on temperature - strain curves for the constraint-aged films in the 2nd thermal cycling (T_{age} = 673 K).

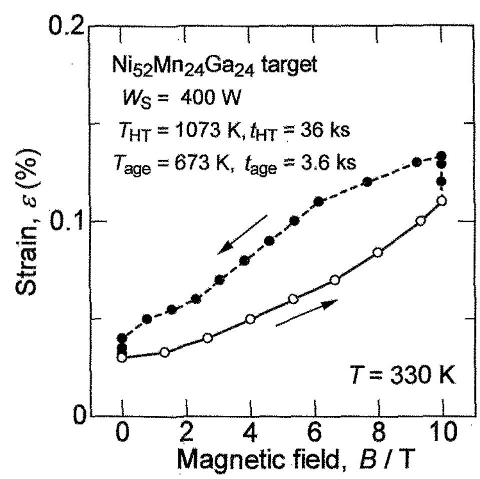

Fig. 7 Magnetic field - strain curve for the constraint-aged film at 330 K (T_{age} = 673 K, t_{age} = 3.6 ks).

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