Shape Memory Behavior of Ni-Mn-Ga Sputtered Films under a Magnetic Field

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The shape memory behavior under the magnetic field up to 5 T was observed in Ni-Mn-Ga sputtered films. The sputtered films were heat-treated at 1073 K for 36 ks for homogenization and aged at 673 K for 14.4 and 56.7 ks in a constraint condition. The martensitic transformation temperatures and Curie temperature of the obtained films were higher than room temperature. The martensitic transformation temperatures increased under a magnetic field. Furthermore, a shape memory effect was observed by increasing and decreasing of the magnetic field.

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1. Introduction

Recently, some ferromagnetic shape memory alloys such as Ni2MnGa, Fe-Pd, Fe-Pt and Ni-Co-Ga have been developed. They are the candidates for the alloys with the shape memory effect under a magnetic field representing the quick response and enabling the remote control. It may solve such problems as low response speed encountered in the Ni
treated at 1073 K for 36 ks for homogenization and aged at 673 K for 14.4 and 56.7 ks in a constraint condition. The martensitic transformation temperatures and Curie temperature of the obtained films were higher than room temperature. The martensitic transformation temperatures increased under a magnetic field. Furthermore, a shape memory effect was observed by increasing and decreasing of the magnetic field.

2. Experiment

2.1 Specimens preparation

Ni-Mn-Ga films were deposited on a poly-vinyl alcohol (PVA) substrate (thickness: 18 μm) with a radio-frequency magnetron sputtering apparatus (Shibaura, CFS-4ES). Two kinds of Ni-Mn-Ga targets whose nominal compositions were Ni52Mn24Ga24 and Ni52.5Mn22Ga25.5 were used. The Ni52.5Mn22Ga25.5 target contained comparatively lower oxygen (~0.1 mass%) than that of Ni52Mn22Ga24. The sputtering power (Wk) was 400 W for the Ni52Mn22Ga24 target and 50 W for the Ni52.5Mn22Ga25.5 target, respectively. The obtained films with a thickness of about 5 μm were heated at 1073 K for 36 ks in vacuum of 2 × 10−4 Pa for homogenization. After the heat treatment, they were bent and put inside a silica tube of 4 mm diameter. The constrained aging was performed at 673 K for 14.4 and 57.6 ks in a flow of argon gas. The compositions of the heat-treated films were determined by the inductively coupled plasma (ICP) spectrometry (Seiko, SPS-1200A). The composition and valence electron concentration (e/a) of the films were shown in Table 1. The valence electrons (e) were assumed to be 3d84s2 (e = 10) for Ni, 3d44s2 (e = 7) for Mn and 4s24p1 (e = 3) for Ga. Hereafter, the composition and the heat treatment of specimens were described as follows,

Table 1 Composition and valence electron concentration (e/a) of the heat-treated films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition of target</th>
<th>Sputtering power (Wk)</th>
<th>Composition of film</th>
<th>Valence electron concentration (e/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N54(HT)</td>
<td>Ni52Mn24Ga24</td>
<td>400 W</td>
<td>Ni53Mn23.5Ga23.0</td>
<td>7.69</td>
</tr>
<tr>
<td>N56(HT)</td>
<td>Ni52Mn22Ga25.5</td>
<td>50 W</td>
<td>Ni56Mn22.5Ga21.8</td>
<td>7.80</td>
</tr>
</tbody>
</table>

*N54(HT), N54(HT-AG57.6), N56(HT), N56(HT-AG14.4), N56(HT-AG57.6)

where N and HT mean the nickel composition and the heat treatment for homogenization at 1073 K for 36 ks, respectively. HT-AG14.4 and HT-AG57.6 mean the constraint-
aging at 673 K for 14.4 and 57.6 ks after HT, respectively. Therefore, the notation of N56(HT-AG57.6) means the specimen of 56 mol% nickel content that was aged at 673 K for 57.6 ks after homogenization at 1073 K for 36 ks.

2.2 Experimental devices

2.2.1 Magnet

A super-conducting magnet (Sumitomo heavy industries, HF%-100VT-50HT) was used to apply the external magnetic field. The shape change under the magnetic field up to 5 T was measured. A bore of the magnet was 50 mm in diameter and a thermostatic bath was set in the bore. The magnetic field was applied parallel to the film surface.

2.2.2 Thermostatic bath

A thermostatic bath was equipped with a thermocouple and a temperature control device for heating and cooling. Temperature homogeneity and stability in this bath was ±0.5 K. The temperature was changed from 290 to 390 K during the measurement. A specimen was set into the thermostatic bath. One end of the specimen was fixed and another end was made free. The upper part of this bath was covered with three glass plates through which the inside was observed.

2.3 Measurement of magnetization and Curie temperature

The magnetization was measured at a magnetic field of 0.1 T by a vibrating sample magnetometer (VSM). The temperature was changed from 283 to 420 K. The mass of the film was about 1 g. The Curie temperature ($T_C$) was determined from the curve changes of the temperature dependence on the magnetization.

2.4 Measurement of shape memory behavior

The shape memory behavior by thermal change was observed using a digital video camera (Sony, DCR-PC120). The measurement was made from 295 to 383 K. Heating and cooling rates were $3.3 \times 10^{-2}$ K/s.

Photographs of the shape change under a magnetic field at various temperatures was taken by a camera with a charge-coupled imaging device (CCD) and recorded on a video tape.

The strain $\varepsilon = (dS/2)/r$, $dS$: thickness of film, $r$: radius of curvature was estimated from the shape change recorded on the video tape.

3. Results and Discussion

3.1 Measurement of magnetization and Curie temperature

The magnetization-temperature curves for (i) N56(HT), (ii) N56(HT-AG14.4), (iii) N56(HT-AG57.6) and (iv) N54(HT-AG57.6) were shown in Fig. 1, respectively. For each film, the magnetization increased during heating and suddenly decreased at the Curie temperature when the ferromagnetic phase disappeared. The Curie temperature of each film was higher than room temperature. It is reported that the strong magnetic anisotropy exists in the martensitic phase at low temperature and the parent phase at high temperature has lower magnetic anisotropy. It is considered that the magnetization at the low magnetic field is small for the martensitic phase and is large for the parent phase. The magnetization increased faintly during heating for the constraint-aged films.

The effect of aging time on the Curie temperature ($T_C$) and the magnetization at room temperature was shown in Fig. 2.

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Fig. 1 Magnetization-temperature curves of (i) N56(HT), (ii) N56(HT-AG14.4), (iii) N56(HT-AG57.6) and (iv) N54(HT-AG57.6).

Fig. 2 Effect of aging time on (i) Curie temperature and (ii) magnetization at room temperature for N56(HT-AG).
$T_C$ and the magnetization of room temperature increased with increasing aging time. It is considered that the degree of order in the martensitic phase increased during constraint-aging and the stress-induced martensitic phase existed in the constraint-aged films.

### 3.2 Shape memory behavior by thermal change

The photographs in Fig. 3 show the shape change of the sputtered film, N56(HT-AG57.6), by the temperature change during heating (a) ~ (d) and cooling (d) ~ (h). The strain-temperature curve by heating and cooling was shown in Fig. 4. Figure 4 shows the two-way shape memory effect by the temperature change during heating from 343 to 367 K and during cooling from 351 to 327 K. This phenomenon corresponds to the two-way shape memory effect, so called all-round shape memory effect. The slopes of heating and cooling curves in the strain-temperature curve were nearly the same.

Figure 5 shows the schematic strain-temperature curve of N56(HT-AG57.6). The inflection temperatures, $A_s^*$, $A_t^*$, $M_s^*$ and $M_t^*$, in the strain-temperature curve during heating and cooling are defined as shown in this figure. $A_s^*$, $A_t^*$, $M_s^*$ and $M_t^*$ resemble $A_s$, $A_t$, $M_s$ and $M_t$, respectively. They mean the start and finish temperatures of shape change by heating and cooling. The transformation temperatures ($A_s^*$, $A_t^*$, $M_s^*$ and $M_t^*$) and Curie temperature ($T_C$) of the various constraint-aged films were listed in Table 2.

Figure 6 shows the effect of the magnetic field (0 and 5 T) in the strain-temperature curves of (i) N54(HT-AG57.6) and (ii) N56(HT-AG57.6), respectively. $A_s^*$, $A_t^*$, $M_s^*$ and $M_t^*$ increased by the magnetic field of 5 T. The shifts of temperature by the magnetic field were 4 and 6 K in N54(HT-AG57.6) and N56(HT-AG57.6), respectively. These films heat-treated under the same condition for HT-AG57.6. N56(HT-AG57.6) showed larger strain and transformation temperature change than N54(HT-AG57.6). Vasil’ev et al. reported that the transformation temperature of a Ni$_2$MnGa single crystal changed by the magnetic field and their strain change by the application of the magnetic field up to 5 T corresponded to that by cooling by 4 ~ 5 K. This result shows the good agreement with the present one.
Therefore, it is considered that the effect of magnetic field on the shape memory behavior will be large at the temperature range between \( A_s^*/C_3 \) and \( A_f^*/C_3 \) on heating, and \( M_s^*/C_3 \) and \( M_f^*/C_3 \) on cooling.

### 3.3 Shape memory behavior by magnetic field change

Figure 7 shows the shape change of N54(HT-AG57.6) under the magnetic field from 0 to 5 T at the temperature between \( A_s^*/C_3 \) and \( A_f^*/C_3 \) on heating, and between \( M_s^*/C_3 \) and \( M_f^*/C_3 \) on cooling. The change of the radius of curvature of the bended film was observed. Figure 7(i) shows the shape change at 323 K between \( A_s^*/C_3 \) and \( A_f^*/C_3 \) on heating, shape change was very small by an increase and a decrease of the magnetic field. Figure 7(ii) shows the shape change at 317 K between \( M_s^*/C_3 \) and \( M_f^*/C_3 \) on cooling, the radius of curvature decreased with an increase of the magnetic field but it did not change by a decrease of the magnetic field.

Figure 8 shows the strain-temperature curve and the strain-magnetic field curves of N54(HT-AG57.6). Figure 8(i) represents the strain-temperature curve, Figs. 8(ii) and (iii) the strain-magnetic field curves at 323 K between \( A_s^*/C_3 \) and \( A_f^*/C_3 \) on heating, and at 317 K between \( M_s^*/C_3 \) and \( M_f^*/C_3 \) on cooling. The symbols of (a) \( \sim \) (d) and (A) \( \sim \) (D) in Fig. 8(ii) and (iii) correspond to the photographs of (a) \( \sim \) (d) and (A) \( \sim \) (D) in Fig. 7. \( T_C \) is indicated in Fig. 8(i). The measurement temperatures are below \( T_C \). The strain-magnetic field curve at 323 K between \( A_s^*/C_3 \) and \( A_f^*/C_3 \) on heating in Fig. 8(ii) changed slightly by an increase and a decrease of the magnetic field. The strain-magnetic field curve at 317 K between \( M_s^*/C_3 \) and \( M_f^*/C_3 \) on cooling in Fig. 8(iii) increased by the increase of the magnetic field up to 2 ~ 5 T and the total strain change was 0.075%. The strain slightly decreased by the decrease of the magnetic field.

The behavior of the shape change by the magnetic field at the temperature between \( A_s^*/C_3 \) and \( A_f^*/C_3 \) on heating is different from that at the temperature between \( M_s^*/C_3 \) and \( M_f^*/C_3 \) on cooling. The strain of the shape change by the magnetic field at the temperature between \( A_s^*/C_3 \) and \( A_f^*/C_3 \) on heating showed small

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Table 2 Martensitic transformation temperatures and Curie temperature of the various constraint-aged films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( A_s^*/K )</th>
<th>( A_r^*/K )</th>
<th>( M_s^*/K )</th>
<th>( M_r^*/K )</th>
<th>( T_C/K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N54(HT-AG56.7)</td>
<td>320</td>
<td>323</td>
<td>314</td>
<td>311</td>
<td>340</td>
</tr>
<tr>
<td>N56(HT-AG14.4)</td>
<td>330</td>
<td>350</td>
<td>340</td>
<td>320</td>
<td>358</td>
</tr>
<tr>
<td>N56(HT-AG56.7)</td>
<td>350</td>
<td>365</td>
<td>349</td>
<td>335</td>
<td>372</td>
</tr>
</tbody>
</table>
change by an increase and a decrease of the magnetic field.
But that at the temperature between \( M_s/C_3 \) and \( M_f/C_3 \) on heating increased with the increase of the magnetic field and did not change largely with the decrease of the magnetic field. This behavior will be expected from the martensitic transformation induced by the magnetic field.

Figures 9 and 10 show the strain-temperature curve and the strain-magnetic field curves of N56(HT-AG14.4) and N56(HT-AG57.6), respectively. The measurements were made at the temperatures between \( A_s^*/C_3 \) and \( A_f^*/C_3 \) on heating, and \( M_s^*/C_3 \) and \( M_f^*/C_3 \) on cooling. In both cases, the strain change was small in (ii) at a temperature between \( A_s^*/C_3 \) and \( A_f^*/C_3 \) on heating, but the total strain change in (iii) at a temperature between \( M_s^*/C_3 \) and \( M_f^*/C_3 \) on cooling was 0.013 and 0.035\% for N56(HT-AG14.4) and N56(HT-AG57.6), respectively. Longer aging time resulted in larger total strain change in Figs. 9(iii) and 10(iii). The total strain change for N54(HT-AG57.6) in Fig. 8(iii) was 0.075\%. It was larger than that for N56(HT-AG57.6).

### 3.4 Correlation between temperature and magnetic field for shape change

In order to investigate the correlation between the temperature and the magnetic field for the shape change, the strain of N56(HT-AG57.6) was measured at sequential temperatures of 347 → 343 → 347 K and by the sequential application of the magnetic field of 0 → 5 → 0 T at 347 K between \( M_s^*/C_3 \) and \( M_f^*/C_3 \) on cooling. The obtained result was shown in Fig. 11.
The total strain change in Fig. 11 was 0.026 and 0.035% for each condition, respectively. It is found that the behavior of the shape change by cooling is similar to that by the applied magnetic field. Hence, it can be concluded that the martensitic transformation was induced by the magnetic field.

As mentioned above, the amount of strain change was small by the relief of the magnetic field at a temperature between \( M_f^* \) and \( M_s^* \) on cooling. It is considered that the martensitic phase generated by the application of the magnetic field did not transform to the parent phase by the relief of the magnetic field and that the driving force is necessary for the reverse transformation. As shown in Fig. 11(i), the recovery of the strain obtained by the temperature change is small. The complete recovery of the strain by the relief of the magnetic field will be attained only in the case that the thermal hysteresis is considerably small.

4. Conclusions

Ni-Mn-Ga sputtered films were prepared by a radio-frequency magnetron sputtering apparatus. After heat-treatment for homogenization and aging in a constrain condition, they exhibited a two-way shape memory effect by the thermal change.

The shape memory effect under a magnetic field up to 5 T at various temperatures was observed for these films. The strain accompanied by the shape change under the magnetic field was evaluated. The martensitic transformation temperatures increased under the magnetic field. Furthermore, the shape memory effect was observed by increasing and decreasing of the magnetic field.

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REFERENCES