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Phase Relations in the Ni–Mn–Ga Ternary System and Aging Effect on Shape Memory Properties of Ferromagnetic Ni_2MnGa Sputtered Films

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Summary. Isothermal sections of the Ni–Mn–Ga ternary phase diagram at 1073 and 1273 K were investigated over a wide range of alloy compositions. The range of the β-Ni_2MnGa phase, its equilibria with the γ-(Mn, Ni), α'-Ni_3Ga, and γ-Ni_3Ga_2 phases, and the liquidus and solidus lines were determined experimentally. The aging effect on the shape memory effect (SME) of Ni_2MnGa sputtered films was also investigated. The two-way SME of the constraint-aged films was confirmed by the temperature change.

Keywords. Nickel–manganese–gallium; Ferromagnetic shape memory alloy; Phase diagram; Shape memory effect.

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 (MT) can be controlled not only by temperature and stress but also by magnetic field [1]. If the SME appears under the magnetic field, its response will be faster than that of the thermal one. Since the MT and *Curie* temperatures change significantly with the alloy composition, these temperatures can be controlled by choosing a suitable composition [2]. It is important to know the range of the austenite phase (β-Ni_2MnGa) in the typical temperature range used for the preparation or annealing of these alloys. The neighboring phases as precipitates in the

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β-Ni_2MnGa phase have significant effects on the SME and the mechanical properties. The phase diagram in the Ni–Mn–Ga system provides a very useful basis for designing the shape memory alloy (SMA).

The use of SMA films for an actuator of micro-machines is very attractive because of its large recovery force and quick response to the magnetic field. The authors have found that the Ni-rich Ni_2MnGa heat-treated films show a one-way SME [3]. Furthermore, a two-way SME by the temperature change has been made by the plastic deformation [3] and the constraint-aging method [4]. Hence, the purpose of the present study is to clarify the phase relations in the Ni–Mn–Ga ternary system in the temperature range normally used for the heat treatment during the preparation of the alloys and the aging effect on the SME of the Ni_2MnGa sputtered films.

Results and Discussions

Phase Relations

Figure 1 shows the isothermal sections of the phase diagram based on the experimental data [5] at 1073 and 1273 K. At 1073 K, the range and the equilibria of the β-Ni_2MnGa, γ-(Mn, Ni), α'-Ni_3Ga, and γ-Ni_3Ga_2 phases have been determined. The isothermal section at 1073 K shows a very broad β-Ni_2MnGa phase. Besides a broad range of γ-(Mn, Ni) phase, the Ni-rich corner of the phase diagram shows the α'-Ni_3Ga and γ-Ni_3Ga_2 phases. With the experimental data at 1273 K, the range and equilibria of the β-Ni_2MnGa, γ-(Mn, Ni), and α'-Ni_3Ga phases have been determined. In comparison with the isothermal section at 1073 K, the range of β-Ni_2MnGa phase is decreased. In the Ni-rich corner, the γ-Ni_3Ga_2 phase is not present at this temperature but the γ-(Mn, Ni) and α'-Ni_3Ga phases are still present and both show only slight changes in the solubility range compared with the section at 1073 K.

SME of the Constraint-aged Films

The changes in composition, MT temperatures, and *Curie* temperature of the Ni-rich Ni_2MnGa sputtered films with the sputtering power have been reported [3]. The composition of the as-deposited film was $Ni_{53.6}Mn_{23.4}Ga_{23.0}$. The MT start and finish temperatures (M_s, M_f) and the reverse MT start and finish temperatures (A_s, A_f) of the heat-treated films were measured by a differential scanning calorimeter (DSC) equipment, and the results were $M_s = 315$ K, $M_f = 311$ K, $A_s = 316$ K, and $A_f = 321$ K. These temperatures are above room temperature.

The SME of the constraint-aged films was investigated. For the SME of the constraint-aged films, the spontaneous shape change is shown in Fig. 2. In the first heating, it changes the shape toward the original straight one before the constraint-aging. As shown in Fig. 2(d), 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. 2(d)–(f)). In the second cooling, the shape at low temperature is nearly the same as that in the first cooling. It is clear from these observations that the film prepared with the constraint-aging method shows the reversible two-way SME by temperature change.

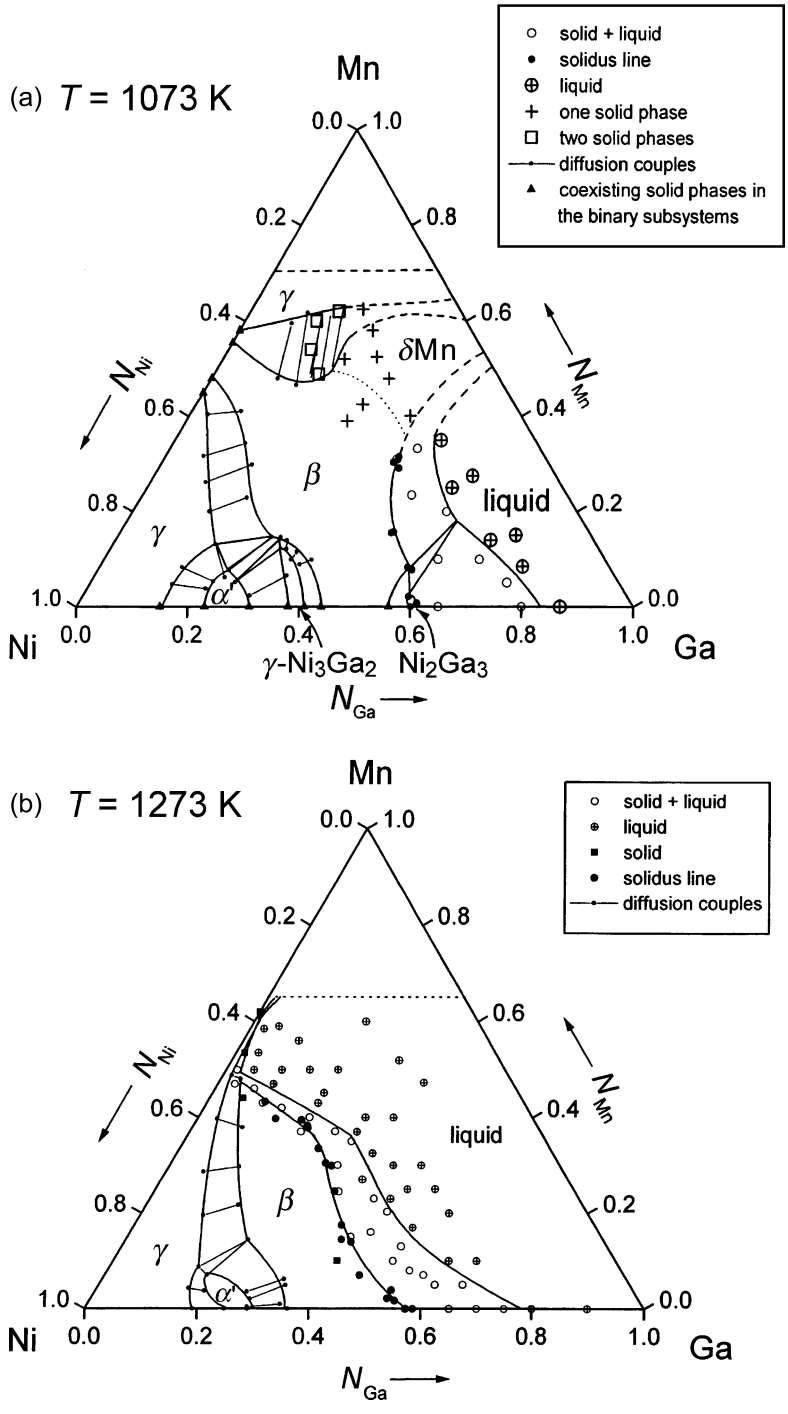

Fig. 1. Isothermal section of the Ni–Mn–Ga ternary phase diagram at (a) 1073 K and (b) 1273 K, respectively (according to Ref. [5])

Figure 3 shows X-ray diffraction (XRD) profiles for the film constraint-aged at 673 K for 0.9 to 57.6 ks. The XRD measurements were made while the films were held at room temperature (RT) and 373 K, respectively. All the films show the

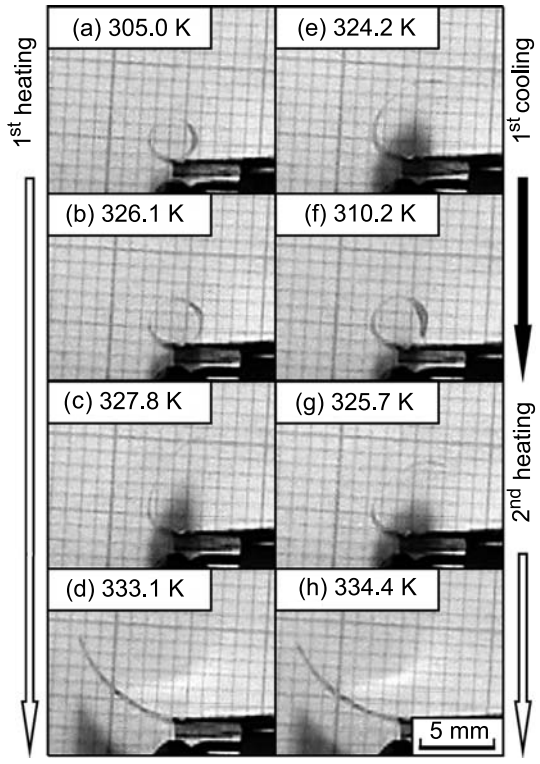

Fig. 2. Two-way shape memory effect of the film constraint-aged at 673 K for 1.8 ks in the 1st heating ((a)–(d)), 1st cooling ((e)–(f)), and 2nd heating ((g)–(h))

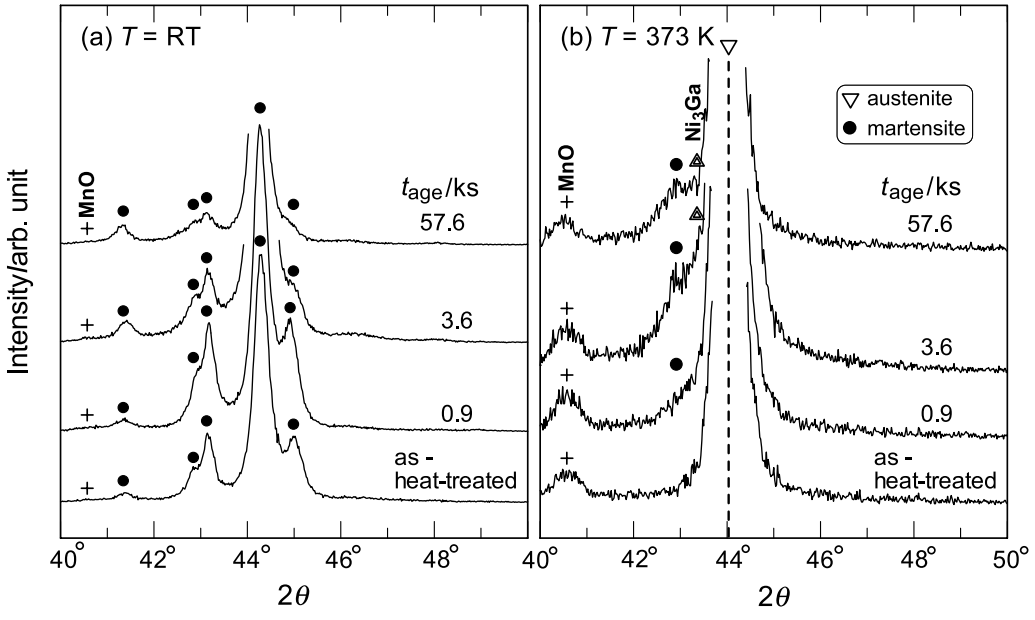

Fig. 3. Effect of aging time on XRD profiles at (a) RT and (b) 373 K for the constraint-aged films, respectively

martensitic structure at RT (Fig. 3(a)). It is found that the martensitic structure of the films changed to the austenitic one through the MT during heating. In addition to the diffraction peaks representing the austenitic phase and the MnO phase, a weak diffraction peak appears around 2θ of 43° in the profiles of all the constraint-aged films. This diffraction peak becomes strong with increasing aging time. Furthermore, a very weak diffraction peak representing the precipitation appears slightly around 2θ of 43.3° in the profiles of the films constraint-aged for 3.6 and 57.6 ks. The precipitation of Mn-contained α'-Ni_3Ga phase with a crystal structure of $L1_2$ has been observed in the long-time constraint-aged film [4]. These results suggest that both the stress-induced martensitic phase and the precipitates exist in the austenitic phase even after heating above A_f and that the inhomogeneous stress fields around them induce the self-accommodation in the martensitic phase under M_s during cooling. 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. The precipitates are also considered to be responsible for it with increasing aging time.

Experimental

Phase Relations

The bulk alloys used in this study were made from commercially available pure 99.99% gallium, 99.99% nickel wire, and 99.9% manganese.

For the determination of the liquidus and solidus lines, the alloys were melted at 1473 K for 7.2 ks and kept at the experimental temperature (1073 or 1273 K) for at least 18 ks. The samples were then quenched in ice water. For the alloys in a solid and liquid two-phase region, the composition of the solid phase was measured by energy dispersion X-ray (EDX) spectroscopy (Hitachi X650S, Kevex 7000Q) to obtain data for the solidus line. The liquidus line was determined by evaluating the solid and liquid two-phase alloys and the single-phase liquid alloy with an optical microscope. The high-temperature phase relations were obtained either by EDX analysis of alloys containing two solid phases or by diffusion couple experiments. The diffusion couples were vacuum sealed in silica tubes and annealed for 7 to 10 days at 1273 K or 5 to 6 weeks at 1073 K.

Preparation of Films

The Ni-rich Ni_2MnGa films were deposited on an alumina substrate (thickness: 0.15 mm) with a radio-frequency (RF) magnetron sputtering apparatus (Shibaura, CFS-4ES) using a $Ni_{52}Mn_{24}Ga_{24}$ target. The sputtering power was 400 W and the substrate temperature was kept at 323 K by cooling water. The thickness of deposited films was about 5 μm. The films were heat treated at 1073 K for 36 ks in a vacuum furnace under 2×10^{-4} Pa. And then, they were mechanically separated form the substrate. Some of the 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 673 K for 0.9–57.6 ks in a flow of argon gas, and then rapidly cooled in air.

Measurements of Properties

The composition of the films was determined by the inductively coupled plasma (ICP) spectrometry (Seiko, SPS-1200A). The MT temperatures of the heat-treated films were measured by a DSC equipment (Perkin-Elmer, Pyris 1). The crystal structure change of the constraint-aged film was identified during heating by an XRD equipment (Rigaku, RAD-C) with Cu Kα radiation. Furthermore, the SME of the 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.

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