Ferromagnetic shape memory alloy Ni_2MnGa films

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Abstract. Heusler type Ni_2MnGa is a ferromagnetic shape memory alloy. Martensitic transformation occurs within the ferromagnetic temperature range. Ni_2MnGa films were fabricated by the melt spinning method and the sputtering method. The physical properties, such as transformation temperatures and magnetic behaviors, of these films was studied. These films had good crystallinity with preferred orientation and showed the crystal structure as same as bulk specimen. Rapidly solidified Ni_2MnGa films made by the single roll melt spinning method have 20 μm in thickness and 1mm in width. Sputtered Ni_2MnGa films were made by using a high frequency magnetron sputtering apparatus. The thickness of the film was 5 μm . The films which were deposited on the poly-vinyl alcohol substrate showed shape memory effect.

1. Introduction

Ferromagnetic Ni_2MnGa occurs martensitic transformation from Heusler type cubic structure of a high temperature phase to a tetragonal one of a low temperature phase within ferromagnetic temperature range during cooling [1]. Single crystal of this material shows the shape memory effect (SME) by heating after deformation at low temperature [2]. Matsumoto *et al.* [3] reported that nonstoichiometric $\text{Ni}_{2-x}\text{Mn}_{1-x}\text{Ga}$ ($x = 0\sim 0.19$) had Heusler type crystal structure and these Curie temperatures decreased and the phase transformation temperatures increased with increase of Ni concentration. These temperatures coincide with each other in high Ni concentration. Vasil'ev *et al.* [4] studied the structural and magnetic transformation. This material is sensitive to the magnetic field. From the results of X-ray diffraction under high magnetic field at low temperature, premartensitic temperature decreased and phase transformation temperatures increase up to 2T and these temperatures were constant from 2 to 5T [5]. Ullakko *et al.* [6] reported that this material shows the large magnetostriction under external magnetic field.

It is discussed that this material has a possibility of SME by magnetic field. If the shape memory alloy (SMA) that operates under magnetic field has been developed, the response of SME will be faster compared to SME by thermal effect and its remote control will be possible. These SMAs will be applied to medical field or micro-actuators. This bulk material is very brittle and it is difficult to make a plate or wire from ingot. A powder metallurgy method is applying to make a workable material [7]. Fabrication and characterization of Ni_2MnGa films are interesting for the study of physical properties and for making micro-actuators. The melt spinning method and the sputtering method were used to make Ni_2MnGa films.

In this paper, the physical properties, such as transformation temperatures and magnetic behaviors, of Ni_2MnGa films made by the melt spinning method and the sputtering method will be reported.

2. Experiment and results

2.1 Specimens preparation

Ni_2MnGa ingot was made by the arc melting method using high purity (above 99.9%) Ni, Mn and Ga. Using this ingot, rapidly solidified Ni_2MnGa films were made by an apparatus of a melt spinning method with a single roll in argon atmosphere. Ribbon shaped films, $20\text{ }\mu\text{m}$ in thickness and 1mm in width, were obtained. The surfaces of films were observed by an optical microscope. The surface contacted to the roll of the apparatus had a structure along the length of ribbon and the reverse surface showed free solidification structure. Heusler type cubic crystal structure of a high temperature phase was observed by X-ray diffraction.

Sputtered Ni_2MnGa films were made by a high frequency magnetron sputtering apparatus. A target was made by Ni, Mn and Ga. Using this target, films were evaporated onto the surface of glass or poly-vinyl-alcohol (PVA) substrates. The concentration of films was affected by high frequency electric power, W_s , and substrate temperature, T_s , in this deposition. After removing PVA substrate, this film, $5\text{ }\mu\text{m}$ in thickness, was annealed at 1073K for 3.6ks .

2.2 Transformation temperatures and magnetic properties

2.2.1 Rapidly solidified film

Temperature change of X-ray diffraction was measured. Figure 1 shows temperature dependence of X-ray diffraction patterns of rapidly solidified Ni_2MnGa film during cooling. During cooling, this cubic

Figure 1. Temperature change of X-ray diffraction patterns of the rapidly solidified Ni_2MnGa film during cooling.

structure changed to tetragonal one by martensitic transformation. The symbols of Cu and Ag in this figure are the diffraction peaks from that of a specimen holder made by copper and adhesive paste containing silver. Using same procedure, temperature dependence during heating was observed. During heating, tetragonal structure at low temperature changed to cubic one. The Differential Scanning Calorimeter (DSC) measurement was performed to detect transformation temperatures. From these results, martensitic transformation start and finish temperatures, M_s and M_f , and reverse transformation start and finish temperatures, A_s and A_f , were determined. They were 120, 90, 125 and 150K, respectively. These temperatures of bulk specimens which have high ordered parameter by long heat treatment were 208, 195, 203 and 218K, respectively. These differences are seemed to be inner strain in film originated by rapid solidification and other reasons. Similar phenomena were observed in rapidly solidified Ti-Pd-Ni system. In this system, transformation temperatures did not increase up to that of bulk specimen by long annealing at high temperature. Large preferred orientation was observed in this diffraction pattern. Curie temperatures of rapidly solidified film and bulk specimen were 349 and 376K, respectively.

2.2.2 Sputtered film

Figure 2 shows X-ray diffraction patterns of sputtered Ni-Mn-Ga film at room temperature. Broad diffraction peaks, (220) and (422), of the as-deposited films on glass and PVA substrates were observed. After annealing at 1073K for 3.6ks, a sharp (200) peak was observed in separation from PVA substrate. Relatively, (422) peak became weak and this shows the large crystal orientation in this annealed film.

The structure of the fracture surface in these films was observed by a scanning electron microscope (SEM). They had columnar grains. In the case of the films deposited on the glass substrate, the width of the columnar grains was 30 and 100nm, corresponding to T_s of 323 and 573K, respectively.

Figure 2. X-ray diffraction patterns of the as-deposited and annealed sputtered Ni-Mn-Ga films.

Figure 3. Temperature change of X-ray diffraction patterns of the sputtered Ni-Mn-Ga films.

Figure 3 shows the temperature change of X-ray diffraction patterns of sputtered film during cooling and heating. By cooling, diffraction peaks from the low temperature tetragonal phase were observed around (220) diffraction peak of a high temperature cubic phase at 236K. In further cooling, diffraction peaks were indexed by the low temperature tetragonal phase. Inversely, during heating, (220) diffraction peak of a high temperature phase was observed in diffraction patterns of the low temperature phase and at the high temperature one, a (220) diffraction peak of the high temperature phase was observed. From the results of temperature change of X-ray diffraction patterns and DSC measurement, M_s , M_f , A_s and A_f were 230, 216, 233 and 250K, respectively.

The temperature changes of magnetization of the sputtered film were measured from 100 to 350K by a SQUID. Figures 4 and 5 show the magnetization vs. temperature curves. External magnetic field was applied parallel and perpendicular to the surface of film. Figure 4 shows the magnetization vs. temperature curves of the films made with W_s of 200 and 400W during heating. The external magnetic field was 8kA/m and applied parallel to the film. Magnetization increased abruptly at around 250K during heating. This temperature corresponded to the reverse martensitic transformation temperature that is in good agreement with the results of DSC measurement. The magnetization in the parent phase of the film made with W_s of 200 and 400W were found to be almost similar. In the martensite phase, magnetization of the film made with W_s of 200 was larger than that of the film made with W_s of 400. Hence, it is considered that the residual parent phase of the film made with W_s of 200W causes the large magnetization compared to that of the film made with W_s of 400W. Figure 5 shows the magnetization vs. temperature curves of the films made with W_s of 200W. The external magnetic field was 8 and 400kA/m and applied parallel and perpendicular to the film. Magnetization was saturated under the external magnetic field of 400kA/m applied parallel to the film, while the saturation magnetization was not observed under the external magnetic field applied perpendicular to the film.

The film, 5 μ m in thickness, was deposited on the PVA substrate. After separated from this substrate, this film was annealed at 1073K for 3.6ks. After bending this flat film by 90 degrees, shape change was observed during heating and flatness was recovered. This is one way shape memory effect.

Figure 4. Magnetization vs. temperature curves of the different sputtered Ni-Mn-Ga films.

Figure 5. Magnetization vs. temperature curves under the different external magnetic fields in the sputtered Ni-Mn-Ga films.

3. Conclusion

Rapidly solidified films and sputtered films were fabricated by the melt spinning method and the sputtering method. Crystal structure was measured by an X-ray diffractometer. Transformation temperatures and magnetic properties were measured by a DSC and a SQUID, respectively. These films have good crystallinity and preferred orientation. Sputtering film has large crystal orientation compared to rapidly solidified one. Magnetization of sputtered films changed at the phase transformation temperature. The magnitude of magnetization in the martensite phase depended on magnitude and direction of the external magnetic field. Magnetization of the films made with W_2 of 200W in the martensite phase at low temperature was saturated under the external magnetic field of 400kA/m applied parallel to the film while the saturation magnetization was not observed under the external magnetic field applied perpendicular to the film.

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