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doi: 10.1063/1.3213353

Martensitic transformation and magnetic field-induced strain in Fe–Mn–Ga shape memory alloy

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(Received 21 July 2009; accepted 7 August 2009; published online 27 August 2009)

Martensitic and magnetic properties of Fe–Mn–Ga single and polycrystalline alloys were investigated. It was found that Fe–Mn–Ga alloys exhibit martensitic transformation from the paramagnetic $L2_1$ Heusler parent phase to the ferromagnetic $L1_0$ martensite phase. The martensitic transformation temperatures increased by about 20 K by the application of a magnetic field of 7 T, and a metamagnetic phase transition was observed. In addition, a magnetic field-induced strain of 0.6% associated with magnetic field-induced forward transformation was confirmed in an $Fe_{43}Mn_{28}Ga_{29}$ single crystal. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3213353]

Since a large magnetic field-induced strain (MFIS) associated with a rearrangement of martensite (M) variants by an external magnetic field in Ni–Mn–Ga alloys was first reported in 1996,[1] many kinds of magnetic shape memory alloy (MSMA) systems, such as Fe–Pd,[2] Fe–Pt,[3] Ni–Mn–Al,[4,5] Ni–Co–Al,[6,7] Ni–Co–Ga,[7,8] and Ni–Fe–Ga,[9] have been reported. Recently, our group has found Ni–Mn–X (X=In, Sn, and Sb) Heusler MSMAs (Ref. 10) characterized by a drastic change in magnetization induced by martensitic transformation from the ferromagnetic parent (P) phase to the paramagnetic M phase.[11,12] The martensitic transformation temperatures of these alloys remarkably decrease with application of a magnetic field, such decrease being brought about by the contribution of Zeeman energy in phase stability between the P and M phases due to the large difference in magnetization. Moreover, it has been reported that a compressive prestrain is recovered by the magnetic field-induced reverse transformation (MFIRT) in Ni–Co–Mn–In single crystal[11,12] and Ni–Co–Mn–Sn polycrystalline alloys.[13] This phenomenon due to the MFIRT, i.e., metamagnetic phase transition, is called the "metamagnetic shape memory effect." The metamagnetic type behavior has also recently been found in Co-doped Ni–Mn–Al (Ref. 14) and Ni–Mn–Ga (Ref. 15) alloys.

Another possibility in magnetic field-induced phase transformation is the magnetic field-induced forward transformation (MFIFT) from a paramagnetic P phase to a ferromagnetic M phase. Kakeshita *et al.*[16–19] reported that the martensitic transformation temperature increases with magnetic field in Fe–Ni, Fe–Ni–C, Fe–Mn–C, and Fe–Pt alloys, but that the shift of the temperature is small, ranging from 0.3 to 2.5 K T^{-1}. It has also been reported in Ni–Mn–Ga alloy that the martensitic transformation temperature increases by 6 K with application of a magnetic field of 1 T. In the MFIFT transformation, specific variants of the M phase, whose easy axis direction is close to the direction of the magnetic field, seem to be preferentially induced by application of a magnetic field, and some MFIS is expected to be obtained. No MFIS due to the MFIFT, however, has been reported, although a strain of 0.82% has been obtained in a stress-assisted condition.[20]

Very recently, the present authors have found martensitic transformation in Fe–Mn–Ga system, where the P phase and M phase are paramagnetic and ferromagnetic, respectively. In this paper, the martensitic and magnetic transformation behaviors of single and polycrystalline Fe–Mn–Ga alloys are reported.

$Fe_{43}Mn_{28}Ga_{29}$ alloy was prepared by induction melting under an argon atmosphere. Polycrystalline specimens were obtained by hot rolling the ingots at 1273 K, removing cracks and cutting the specimens into small pieces. A single crystal with dimensions of $1.085\times1.090\times2.205$ mm^3, $\langle100\rangle_P$ directions being parallel to the faces, was obtained using grain growth by annealing the ingot at 1273 K for 168 h. Single and polycrystalline alloys were annealed at 1273 K for 2 h, followed by quenching in ice water. The microstructure was observed by optical microscopy, and the martensitic transformation temperatures were measured by differential scanning calorimetry (DSC) at heating and cooling rates of 5 K min^{-1}. The magnetic properties were examined using a superconducting quantum interference device at heating and cooling rates of 2 K min^{-1}. The MFIS in the longitudinal direction of the single crystal, to which the magnetic field was applied, was measured by a three-terminal capacitance method.

DSC cooling and heating curves for an $Fe_{43}Mn_{28}Ga_{29}$ polycrystalline alloy are shown in Fig. 1. Exothermic and endothermic peaks are detected during cooling and heating, respectively, which correspond to the forward and reverse martensitic transformations, respectively. The martensitic transformation starting (M_s), finishing (M_f), reverse transformation starting (A_s) and finishing (A_f) temperatures defined, as shown in Fig. 1, are M_s=213 K, M_f=162 K, A_s=231 K, and A_f=294 K, respectively, and a large thermal hysteresis of about 70–80 K is confirmed. The optical micrograph of the martensite phase at 133 K is also shown in Fig. 1, where the morphology is similar to the plate type of the α' (bcc or bct) martensite in conventional Fe-based alloys. The crystal structures for the P and M phases in the $Fe_{43}Mn_{28}Ga_{29}$ alloy were identified as being $L2_1$ (Heusler)

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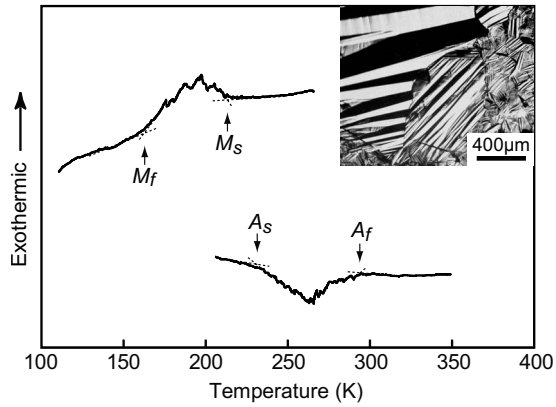

FIG. 1. (a) DSC curves during cooling and heating and microstructure of martensite phase at 133 K in $Fe_{43}Mn_{28}Ga_{29}$ polycrystalline alloy.

and $L1_0$ (which is commonly used, but strictly speaking, it is $D0_{22}$) using an x-ray diffraction technique, the lattice parameters of which are $a_0=0.5864$ nm and $a=0.3805$ nm and $c=0.3529$ nm (0.7058 nm), respectively. Here, the c/a of the $L1_0$ phase is about 0.927 and the volume change due to the forward transformation ΔV is about +1.35%. In many martensite alloys showing thermoelastic transformation, the volume change ranges from −0.1% to −0.5%.[21] Therefore, the large positive volume change in the transformation may be one of the reasons for the large thermal hysteresis. It is very interesting to note that while the martensitic transformation in usual Fe-based alloys, including the Fe–C, Fe–Ni, and Fe–Mn alloys, takes place from the fcc P phase to the bcc (bct) or hcp M phase, that in the present Fe–Mn–Ga alloys is from the bcc P phase to the fct M phase. The details of the phase stability and the magnetic property will be discussed elsewhere.

Figure 2(a) shows the thermomagnetization curve of the $Fe_{43}Mn_{28}Ga_{29}$ polycrystalline alloy for cooling and heating at magnetic field strengths of $H=0.05$ and 7 T. During the first cooling under a magnetic field of $H=0.05$ T, the magnetization increases at temperatures between 200 and 130 K, corresponding to the martensitic transformation, and a decrease in the magnetization during heating is induced by the reverse martensitic transformation. The magnetism of the P and M phases is considered to be paramagnetic and ferromagnetic, respectively. It is interesting to note that the bcc and fcc phases in Fe alloy are normally ferromagnetic and

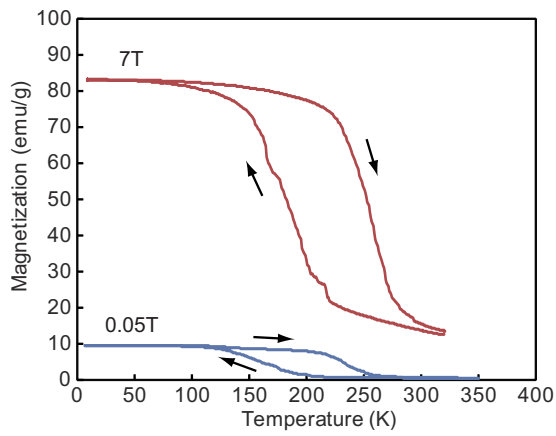

FIG. 2. (Color online) Thermomagnetization curves of $Fe_{43}Mn_{28}Ga_{29}$ polycrystalline alloy under magnetic field strengths of $H=0.05$ and 7 T.

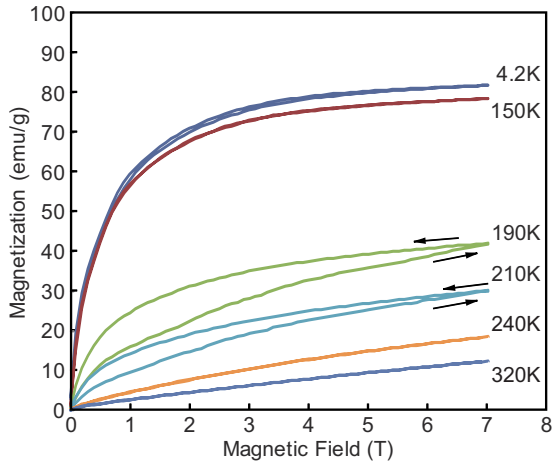

FIG. 3. (Color online) Magnetization curves of $Fe_{43}Mn_{28}Ga_{29}$ polycrystalline alloy at various temperatures between 4.2 and 320 K.

paramagnetic or antiferromagnetic, respectively; however, the Fe–Mn–Ga alloy exhibits the opposite. In the thermomagnetization curve under a magnetic field strength of 7 T, the martensitic transformation temperatures increase by about 20 K by application of a magnetic field. It has been reported[11] that in the $Ni_{45}Co_5Mn_{36.6}In_{13.4}$ metamagnetic shape memory alloy the shift of the transformation temperature for 7 T is $\Delta T=-30$ K, where the direction in the shift of temperature is in reverse. This difference of the shifting direction is attributed to the difference in the magnetism of the P and M phases between these alloys. The ΔT induced by a magnetic field change ΔH is approximately given by the Clausius–Clapeyron relation in the magnetic phase diagram

$$\Delta T \approx -(\Delta I/\Delta S)\Delta H, \tag{1}$$

where ΔI and ΔS are the difference in magnetization and entropy between the P and M phases, respectively. The theoretical value of ΔT for $\Delta H=7$ T calculated from Eq. (1) is 26 K, where $\Delta I=-62$ emu g^{-1} and $\Delta S=16.4$ J K^{-1} kg^{-1} experimentally determined in Figs. 2 and 1, respectively, are used. This calculation is in agreement with the experimental result.

Magnetization curves of the $Fe_{43}Mn_{28}Ga_{29}$ polycrystalline alloy at various temperatures are shown in Fig. 3, where the measurements at temperatures between 190 and 240 K were conducted by careful cooling from the P phase. While the curves at 240 and 320 K and at 4.2 and 150 K exhibit typical paramagnetic and ferromagnetic properties, respectively, a metamagnetic phase transition is observed at 190 and 210 K with hysteresis, which is considered to be due to the MFIFT from the paramagnetic P phase to the ferromagnetic M phase as expected from the thermomagnetization curves shown in Fig. 2.

Shown in Fig. 4 is the relative length change $\Delta L/L$ of the $Fe_{43}Mn_{28}Ga_{29}$ single crystal parallel to the magnetic field direction applied to the $[100]_P$ at 240 K, almost the same as the M_s temperature ($M_s^{sc}=246$ K) for the single crystalline specimen. During the application of a magnetic field, shrinkage starts to be detected at 2 T and there in an abrupt change at around 3.5 T, and the total strain becoming 0.6% at 8 T, with some fluctuation. No reversible length change appears by removing the magnetic field. This phenomenon, which is nearly three times as large as the giant magnetostriction of Terfenol-D, is apparently due to the MFIFT. Considering the

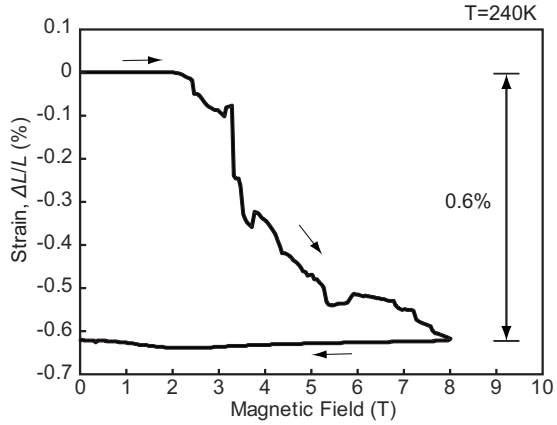

FIG. 4. Magnetic field-induced strain in the direction parallel to the magnetic field applied in the [100] direction of the parent phase at 240 K in $Fe_{43}Mn_{28}Ga_{29}$ single crystal.

lattice parameters and lattice correspondence, the shape change caused by the martensitic transformation is 20.6% expansion in the $[001]_P$ direction and 8.2% shrinkage in the $[100]_P$ and $[010]_P$ directions. In this transformation, specific variants of the *M* phase, whose easy axis direction is close to the direction of magnetic field, may be preferentially induced by application of a magnetic field and some MFIS can be detected, the shrinkage of the MFIS suggesting that the *c* plane is the magnetic easy axis in the *M* phase. The small value of the MFIS is explained by the fact that the MFIFT by 7 T is only partial, as shown in Fig. 3, and the fluctuation appearing in the magnetostriction curve may result from the coexistence of the *M* variants along the noneasy axis. This new type of MFIS is comparable to the usual superelasticity induced by stress. Therefore, in contrast with the Ni–Mn–*X* (*X*: In, Sb, and Sn) metamagnetic shape memory alloys, a perfect reversible strain without bias force is possible when a magnetic field over a critical strength for martensitic transformation is applied above the reverse martensitic transformation temperature, although a small thermal hysteresis of martensitic transformation is required to reduce the critical magnetic field. Thus, the Fe–Mn–Ga alloy system is promising for new functional materials.

In conclusion, it was found that Fe–Mn–Ga alloys exhibit martensitic transformation from the paramagnetic *P* phase with the $L2_1$ structure to the ferromagnetic *M* phase with the $L1_0$ structure and that the martensitic transformation temperatures increase by about 20 K by the application of a magnetic field of 7 T. A metamagnetic phase transition was also observed, and a strain of 0.6% was confirmed due to the MFIFT in an $Fe_{43}Mn_{28}Ga_{29}$ single crystal. Consequently, Fe–Mn–Ga alloys should be categorized as magnetic shape memory alloys showing some MFIS.

This study was supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS) and by the Global COE Program "Materials Integration (International Center of Education and Research), Tohoku University," MEXT, Japan. The authors would like to thank Professor A. Fujita of the Graduate School of Engineering, Tohoku University for measurements of the magnetostriction. A part of this work was carried out at the Center for Low Temperature Science, Institute for Materials Research, Tohoku University.

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