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Control of Phase Transformation Temperatures by Substituents in Ni-Fe-Ga Ferromagnetic Shape Memory Alloys

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The variations of the martensitic transformation starting temperature $T_M{}^S$ and the Curie temperature T_C in Ni-Fe-Ga alloys have been investigated by substituting with several kinds of the fourth elements. By partial substitution of Co or Cu for Ni, T_C increases and $T_M{}^S$ decreases. In particular, the increase of T_C is remarkable in the $Ni_{54-x}Co_xFe_{19}Ga_{27}$ alloy, which is related to the strong Ni-Co and Co-Fe exchange interactions. For the $Ni_{54}Fe_{19-x}Mn_xGa_{27}$ alloys, T_C slightly increases with the increase of Mn content, in analogy with the $Ni_{52}Fe_xMn_{21-x}Ga_{27}$ alloys. From the present study, it is demonstrated that both T_C and $T_M{}^S$ of the Ni-Fe-Ga alloys can be effectively controlled by selecting the substituents. [doi:10.2320/matertrans.MI200714]

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1. Introduction

In ferromagnetic shape memory alloys (FSMAs), the thermoelastic martensitic transformation in the ferromagnetic state is controlled by external magnetic fields. Compared with the conventional thermally induced shape memory alloys, the magnetic-field induced shape memory alloys have an advantage in a rapid response to the input signal, because the response against temperature change is limited by thermal conductivity of materials. In addition, large magnetic-field-induced strains (MFISs) have been observed in the martensite phase of FSMAs such as Ni_2Mn(Ga, Al),[1–5] Fe(Pt, Pd),[6,7] and CoNi(Ga, Al) alloys.[8–11] Fast responses and large MFIS of FSMAs are also indispensable for applications to various sensors and actuators.

MFISs arise from the motion of variant boundaries in the martensite phase.[1,2] In the martensite phase of FSMA, the magnetocrystalline anisotropy energy E_k is large due to its low symmetry of the crystal structure.[12] In each martensite variant, the magnetic moment is pinned to the magnetic easy axis due to a large E_k as reported by Murakami *et al.*[13] When E_k is larger than the driving energy necessary to move variant boundaries, the variants are replaced to other variants so that the magnetic easy axis becomes nearly parallel to the applied field direction. Accordingly, a large magnetocrystalline anisotropy constant is necessary to obtain a large MFIS.

Recently, new Ni-Fe-Ga FSMAs were developed by our group[13–18] and have attracted much attention. These alloys undergo a thermoelastic martensitic transformation.[14,15] In addition, it has been demonstrated that $Ni_{54}Fe_{19}Ga_{27}$ alloy in the martensite phase exhibits a large magnetocrystalline anisotropy constant $K = 1.8 \times 10^6\,\mathrm{erg/cm^3}$ at low temperatures.[17] However, the value of K in the vicinity of room temperature is reduced because of a relatively low Curie temperature $T_C = 310\,\mathrm{K}$.[17] In order to utilize the MFIS as magnetostrictive devices at room temperature, increases of T_C by partial substitutions of Co have been attempted.[19–22] As expected, T_C is increased to 405 K by substitution of 6% Co for Ni in $Ni_{55}Fe_{18}Ga_{27}$ alloy with $T_C \sim 290\,\mathrm{K}$[15,19,22] and hence the single-variant martensite phase of $Ni_{49}Fe_{18}Ga_{27}Co_6$ exhibits a relatively large K of about $1.2 \times 10^6\,\mathrm{erg/cm^3}$ at 300 K,[22] resulting in MFIS of 8.5%.[22] However, the partial substitution of 6% Co leads to the decrease of the martensitic transformation temperature $T_M{}^S$ down to 300 K.[19,22] Consequently, the MFIS disappears at room temperature by further substitution of Co, because the MFIS is obtained in the martensite phase. Therefore, systematic studies for influence of various substitution elements on $T_M{}^S$ and T_C in Ni-Fe-Ga FSMA alloys are necessary to obtain more large MFISs at room temperature.

In the present study, the effect of partial substitution of Co on $T_M{}^S$ and T_C have been investigated for $Ni_{54-x}Co_xFe_{19}Ga_{27}$ alloys, which exhibit much higher T_C compared to previously studied $Ni_{55-x}Co_xFe_{18}Ga_{27}$ due to a higher Fe concentration. Furthermore, it has been reported that T_C increases by partial substitution of Cu[23,24] and Mn[25,26] in Ni_2MnGa alloy. Accordingly, Co, Cu and Mn were selected as substituents in the present study.

2. Experiment

Various polycrystalline Ni-Fe-Ga-X (X = Co, Cu, and Mn) alloys for measurement were prepared by arc melting in an argon gas atmosphere. The specimens were annealed at 1453 K for 24 h for homogenization, followed by quenching in ice water. After homogenization, to achieve atomic order in the Heusler structure, the specimens were annealed at 773 K for 24 h in a vacuum quartz tube. In order to determine the martensitic transformation starting temperature $T_M{}^S$ and the Curie temperature T_C, the thermomagnetizations were measured in a magnetic field of 40 kA/m in the cooling process by using a superconducting quantum interference device (SQUID) magnetometer and a vibrating sample magnetometer (VSM).

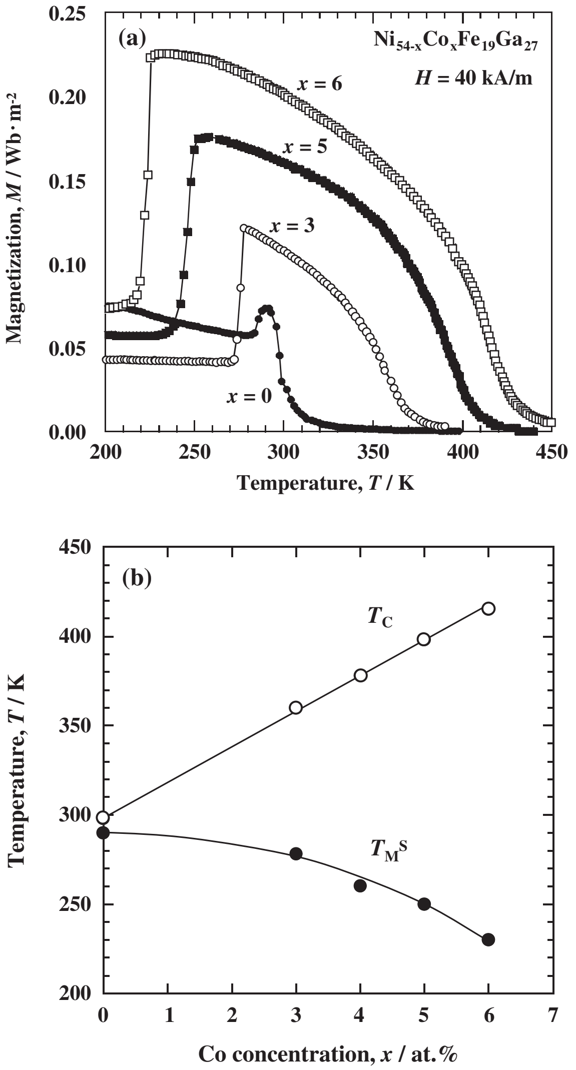

Fig. 1 Magnetic and martensitic properties of the $Ni_{54-x}Co_xFe_{19}Ga_{27}$ ($x = 0\sim6$) alloys. (a) thermomagnetization curves in a magnetic field of 40 kA/m in the cooling process, (b) the Curie temperature T_C and the martensitic transformation starting temperature $T_M{}^S$ as a function of the Co concentration.

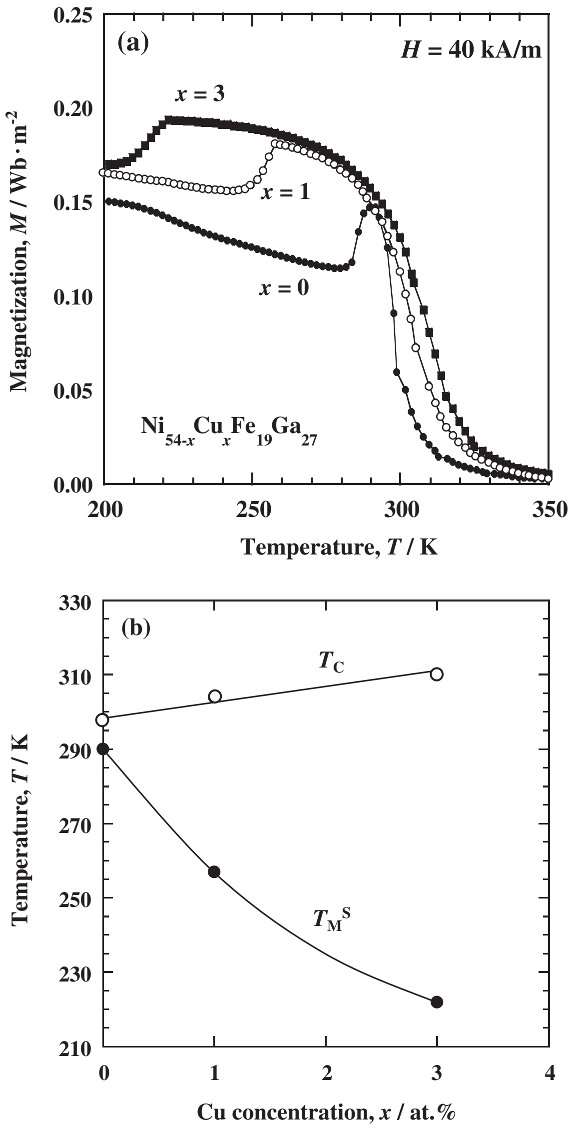

Fig. 2 Magnetic and martensitic properties of the $Ni_{54-x}Cu_xFe_{19}Ga_{27}$ ($x = 0$, 1 and 3) alloys. (a) the thermomagnetization curves in a magnetic field of 40 kA/m in the cooling process, (b) the Curie temperature T_C and the martensitic transformation starting temperature $T_M{}^S$ as a function of the Cu concentration.

3. Results and Discussion

Thermomagnetization curves of $Ni_{54-x}Co_xFe_{19}Ga_{27}$ ($x = 0$, 3, 5 and 6) alloys are presented in Fig. 1(a). From the thermomagnetization (M-T) curves in Fig. 1(a), both T_C and $T_M{}^S$ of each alloy were determined. During the cooling process, there is a remarkable increase of magnetization M below T_C, and a drastic decrease of M at further low temperature due to the martensitic transformation. In the present study, T_C is conventionally defined as the minimum point of the derivative of magnetization dM/dT, and $T_M{}^S$ is defined as the temperature where the value of M decreases drastically. From these results, the concentration dependences of T_C and $T_M{}^S$ are plotted in Fig. 1(b). In the cooling process, the phase of each alloy changes from the paramagnetic parent to the ferromagnetic parent, and finally changes to the ferromagnetic martensite. In $Ni_{54-x}Co_xFe_{19}Ga_{27}$, T_C increases from 360 K to 415 K, whereas $T_M{}^S$ decreases with increasing Co content x from 3 to 6 as seen in Fig. 1(b). These trends are similar to those of Oikawa *et al.*[20] and Morito *et al.*[22] Recently, Kurtulus *et al.* calculated the exchange interaction between transition elements in Heusler alloys X_2MnZ (X = Co, Ni, Cu, Ph and Pd, Z = Ga, Si, Ge and Sn).[27] According to their calculations, T_C is influenced by a stronger X-Mn nearest neighbor exchange interaction as compared with the Mn-Mn one. Therefore, the observed increase of T_C in the Ni-Co-Fe-Ga alloys implies that the magnitude of the exchange interactions of Co-Ni and Co-Fe is larger than that of the Ni-Fe.

Figure 2(a) shows the M-T curves for the $Ni_{54-x}Cu_xFe_{19}Ga_{27}$ ($x = 0$, 1 and 3) polycrystalline specimens. Although Cu is a nonmagnetic element, T_C slightly increases by partial substitution. On the other hand, the decrease of $T_M{}^S$ is significant in comparison with the partial substitution of Co. In Ni_2MnGa alloy, it is suggested that the increase of T_C is attributed to the increase of magnetic

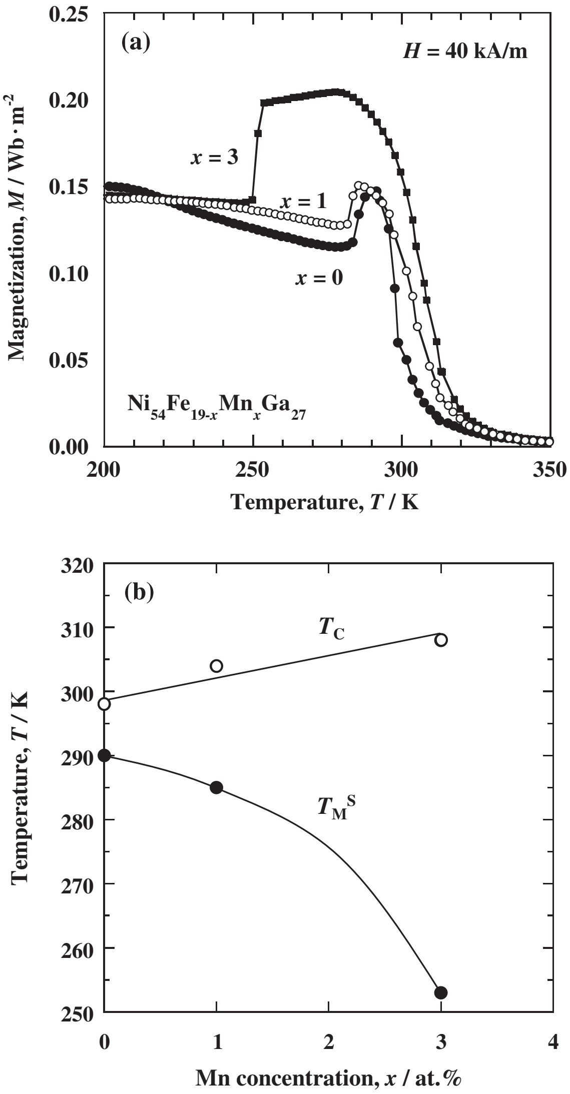

Fig. 3 Magnetic and martensitic properties of the $Ni_{54}Fe_{19-x}Mn_xGa_{27}$ ($x = 0$, 1 and 3) alloys. (a) the thermomagnetization curves in a magnetic field of 40 kA/m in the cooling process, (b) the Curie temperature T_C and the martensitic transformation starting temperature $T_M{}^S$ as a function of the Mn concentration.

moment of Mn atom due to a narrowing of the Mn d-band.[24) In the present $Ni_{54-x}Cu_xFe_{19}Ga_{27}$ alloys, the saturation magnetization at 4.2 K determined from magnetization curve increases from 56.3 to 57.0 emu/g with increasing Cu content x from 0 to 3. Furthermore, the value of T_C determined from Fig. 2(a) increases from 298 K to 309 K with increasing Cu content x from 0 to 3 as given in Fig. 2(b). From these results, the increase of T_C may be concerned with the enhancement of magnetic moment of Fe in analogy with Ni_2MnGa alloy. More detailed discussion on the relation between the Fe magnetic moment and T_C is necessary.

The M-T curves for $Ni_{54}Fe_{19-x}Mn_xGa_{27}$ ($x = 0$, 1 and 3) polycrystalline alloys are given in Fig. 3(a), and T_C and $T_M{}^S$ are shown in Fig. 3(b). From the M-T curves in Fig. 3(a), both T_C and $T_M{}^S$ of each alloy were determined. With increasing Mn content x from 0 to 3, T_C slightly increases from 298 K to 308 K, whereas $T_M{}^S$ decreases. The present tendency is consistent with that of Kikuchi *et al.*[25) and Tsuchiya *et al.*[26) In their studies, the effect of partial substitution of Mn by Fe in $Ni_{52}Mn_{21-x}Fe_xGa_{27}$ on T_C was investigated. For $Ni_{52}Mn_{21-x}Fe_xGa_{27}$ alloy, T_C increases with increasing x and then has a maximum around $x = 15$ mol%.[26)

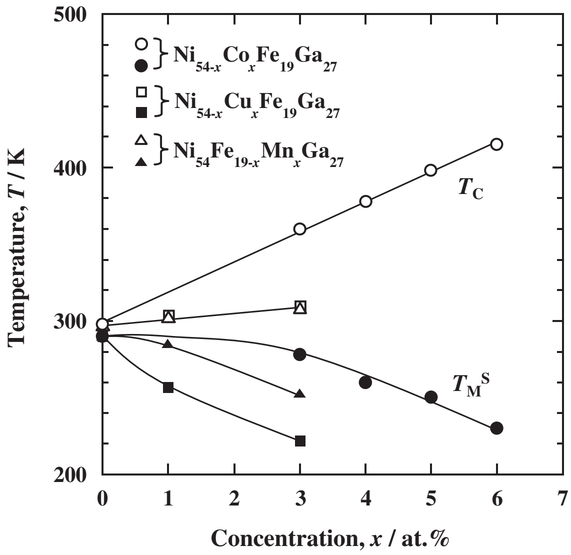

Fig. 4 Concentration dependences of the Curie temperature T_C and the martensitic transformation starting temperature $T_M{}^S$ of the $Ni_{54-x}Co_xFe_{19}Ga_{27}$, $Ni_{54-x}Cu_xFe_{19}Ga_{27}$ and $Ni_{54}Fe_{19-x}Mn_xGa_{27}$ alloy systems. The open and closed symbols stand for T_C and $T_M{}^S$, respectively.

The concentration dependences of T_C and $T_M{}^S$ for $Ni_{54-x}Co_xFe_{19}Ga_{27}$, $Ni_{54-x}Cu_xFe_{19}Ga_{27}$ and $Ni_{54}Fe_{19-x}Mn_x$-Ga_{27} are summarized in Fig. 4. For all the alloy systems, T_C increases, whereas $T_M{}^S$ decreases with increasing x. It should be noted that the increase of T_C is remarkable and value of $T_M{}^S$ is relatively high in the $Ni_{54-x}Co_xFe_{19}Ga_{27}$ alloy, compared with those of the other alloys, and T_C of 415 K for the $Ni_{48}Co_6Fe_{19}Ga_{27}$ alloy is higher than that for the $Ni_{49}Co_6Fe_{18}Ga_{27}$ alloy. From the present results, it is clear that both T_C and $T_M{}^S$ of the Ni-Fe-Ga alloys can be effectively controlled by selecting appropriate substituents.

4. Conclusion

Controls of the Curie temperature T_C and the martensitic transformation starting temperature $T_M{}^S$ in Ni-Fe-Ga alloys were investigated by substituting several kinds of elements. By partial substitution of Co or Cu for Ni, T_C increases and $T_M{}^S$ decreases. The $Ni_{54}Fe_{19-x}Mn_xGa_{27}$ alloys also exhibit similar tendencies, though the effects are moderate. The effect on T_C is remarkable in the $Ni_{54-x}Co_xFe_{19}Ga_{27}$ alloy, increasing from 360 K to 415 K with increasing Co content x from 3 to 6. On the other hand, Cu in the $Ni_{54-x}Cu_xFe_{19}Ga_{27}$ is effective for decreasing $T_M{}^S$. Accordingly, both T_C and $T_M{}^S$ of the Ni-Fe-Ga alloys can be controlled by selecting appropriate substituents.

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