Materials Transactions, Vol. 43, No. 9 (2002) pp. 2360 to 2362

EXPRESS RAPID PUBLICATION

Magnetic and Martensitic Phase Transformations in a $Ni_{54}Ga_{27}Fe_{19}$ Alloy

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The martensitic and magnetic transitions of $Ni_{54}Ga_{27}Fe_{19}$ alloy were investigated by differential scanning calorimetry and X-ray powder diffraction and with a vibrating sample magnetometer. The alloy is martensitically transformed from a $L2_1$ to a martensite phase with a 14M (7R) structure. The ferromagnetic transition is also accompanied by the martensitic transformation from a paramagnetic parent phase to a ferromagnetic martensite phase in the temperature interval between M_s (= 293 K) and M_f (= 274 K). The Ni–Ga–Fe system is promising as a ferromagnetic shape memory alloy.

(Received July 22, 2002; Accepted August 12, 2002)

Keywords: *ferromagnetic shape memory alloy, martensitic transformation, nickel–gallium–iron alloy, phase diagram*

1. Introduction

Ferromagnetic shape memory alloys (FSMAs) showing the displacive transformation in the ferromagnetic state have a possibility of inducing the thermoelastic martensite transformation and rearrangement of martensite variants by applying the external magnetic field. Since a large magnetically induced stain was confirmed in Ni_2MnGa Heusler alloys,[1)] extensive studies have been conducted to develop new ferromagnetic shape memory alloys, such as Fe–Pd,[2)] Fe_3Pt alloys,[3)] Ni_2MnAl[4,5)] and CoNiGa alloys.[6,7)]

Recently, the present authors have developed new ductile FSMAs with a β phase in Co–Ni–Al[8,9)] and Co–Ni–Ga[6)] ternary alloy systems. Since the composition range of the β phase alloy having the FSM is located near the $\beta/\beta+\gamma$ phase boundary, the γ (A1: disordered fcc) phase which results in the significant improvement of ductility can be introduced in the β-based alloys by suitable choices of the alloy composition and the annealing condition.

The martensite starting temperature (M_s) of the β phase in the Co–Ni–Al and Co–Ni–Ga systems decreases with increasing Co and Al or Ga content, whereas the Curie temperature and the spontaneous magnetization increase with increasing Co content and with decreasing Al or Ga content. It is considered that the ferromagnetism of these alloys is closely correlated with Co antistructure atoms on the Al or Ga sites.

In the Fe–Ga binary system, the ferromagnetic B2 and $D0_3$ phases appear in a wide range of composition at temperatures over 892 K.[10)] Since the NiGa B2 phase is stable in wide ranges of temperature and composition,[11)] the solid solution of (Ni, Fe)Ga B2 phase is formed at a high temperature. Furthermore, a doping of Fe to the Ni-rich NiGa β phase alloys is expected not only to induce the ferromagnetism in a similar manner as an Fe doped Ni_3Ga $L1_2$ phase[12)] but also to exhibit the thermoelastic martensitic transformation just as Co–Ni–Ga B2 alloys.[6)] The present study has been undertaken to investigate the magnetic transition and the martensitic transformation of a $Ni_{54}Ga_{27}Fe_{19}$ β phase alloy.

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2. Experiment

$Ni_{54}Ga_{27}Fe_{19}$ (at%) alloy weighing about 20 g was prepared by a cold crucible levitation melting method, and was cast into a copper mold. Some small pieces of the specimen were taken from the ingot and sealed in a quartz capsule filled with an argon gas. The solution heat treatment was conducted at 1473 K for 10.8 ks and quenched into ice water. The microstructure of the specimen was examined by optical microscopy. The Curie temperature T_C and the magnetization M were measured with a vibrating sample magnetometer (VSM), and the martenstitic transformation temperatures were determined by differential scanning calorimetry (DSC) with the cooling and heating rates of 10 K/min.

Phase identification and characterization were carried out by X-ray powder diffraction (XRD) using Cu–Kα radiation. The solution treated powder was sealed in a quartz capsule and heat treated at 1473 K for 0.9 ks. After heat treatment, the capsule was dropped into ice water.

3. Results and Discussion

3.1 Microstructures and martensitic transformation temperatures

The optical micrograph at room temperature is shown in Fig. 1. A typical twinned martensitic structure is observed in some regions. This result implies that the transformation temperatures are located in the vicinity of room temperature. Figure 2 shows the DSC curves, where the endothermic and exothermic reactions corresponding to the martensitic transformations were observed upon heating and cooling processes, respectively. The martensitic temperatures (M_s = 293, M_f = 274, A_s = 292 and A_f = 308 K) were defined as the cross points of the base line and the tangent of the maximum or minimum inclination in the DSC curves as given in Fig. 2. Since the transformation hysterisis (T_h, $A_f - M_s$ = 15 K) is very small, the transformation is expected to be thermoelastic, exhibiting a shape memory effect. Both the transformation enthalpy and the entropy determined from the DSC curves are about ΔH = 340.28 J/mol

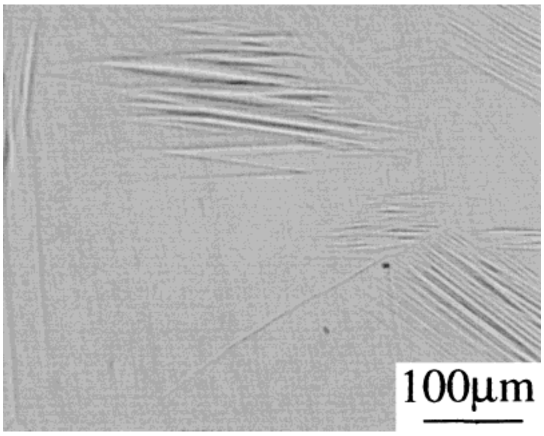

Fig. 1 Room temperature optical micrographs of $Ni_{54}Ga_{27}Fe_{19}$ alloy.

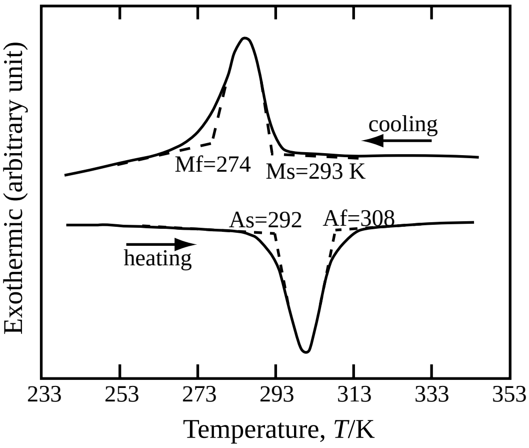

Fig. 2 DSC curves of $Ni_{54}Ga_{27}Fe_{19}$ alloy.

and $\Delta S = 1.13$ J/mol·K, respectively.

Figure 3 are the XRD patterns obtained at room temperature and at 203 K. The spectrum peaks of the parent phase obtained at room temperature are identified well as a BCC structure as indexed in Fig. 3. No extra characteristic peaks of the ordered structures, such as B2, $D0_3$ existing in the Fe–Ga and Ni–Ga binary systems,[10] were clearly confirmed from the XRD result, because the atomic scattering factors of Fe, Ni and Ga are close one another. The crystal structure of the parent phase at room temperature was identified as the $L2_1$ Heusler type by transmission electron microscopic (TEM) examination. Furthermore, the dark field image taken from the $(111)_{L2_1}$ super-lattice reflection showed small anti-phase domains (APDs) with several decades nanometer in diameter, while no APD structure was observed in that from the $(200)_{L2_1}$ reflection. This fact suggests that the parent phase with the B2 structure at the annealing temperature of 1473 K transforms to the $L2_1$ structure during quenching. Details of the TEM examination will be presented in the separate paper.[13] Weak spectra matched with those of disordered fcc (γ) phase were also observed, although no γ phase was confirmed in the bulk sample by the optical microscopic observation. The γ phase probably precipitates during the cooling process, because the cooling rate from the heat treatment temperature of the powder without breaking the quartz tube is slower than that of the quenched bulk sample. The X-ray diffraction lines at 203 K for the martensite phase are identified well as

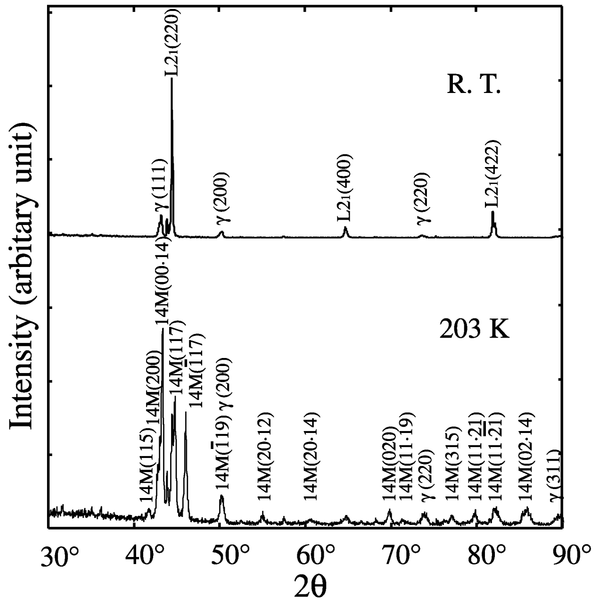

Fig. 3 X-ray diffraction spectra of the parent phase at room temperature and martensite phase 203 K for $Ni_{54}Ga_{27}Fe_{19}$ alloy.

a 14M (7R) structure as indexed in Fig. 3. The lattice parameters have been determined for the martensite phase as $a_{14M} = 0.427$ nm, $b_{14M} = 0.270$ nm, $c_{14M} = 2.930$ nm and $\beta_{14M} = 86.6°$. The 14M martensite phase was observed in NiAl β phase binary[14] and its ternary alloys.[15–18] According to the corresponding lattice constants between the $L1_0$ and 14M structures, the c/a_{L1_0} of the $L1_0$ structure is given by $c/a_{L1_0} = \sqrt{a_{14M}^2 - b_{14M}^2}/\sqrt{2}b_{14M}$.[18] The ratio of c/a_{L1_0} calculated from a_{14M} and b_{14M} is 0.866, very close to that ($c/a = 0.865$) of $Ni_{57}Al_{25}Fe_{18}$ alloy.[19]

3.2 Magnetic transition

Figure 4(a) shows the thermomagnetization curves in a magnetic field of 0.04 MAm^{-1} on heating and cooling process for $Ni_{54}Ga_{27}Fe_{19}$ alloy. The curves exhibit a clear hysteresis, implying that this ferromagnetic transition is of a first-order transition. Figure 4(b) shows the temperature derivative of magnetization, $\partial M/\partial T$, for the thermomagnetization curve in Fig. 4(a). When the transition temperatures are defined as the cross point of the base line and the tangent of the maximum inclination as shown in Fig. 4(b), the transition temperatures ($M_s = 289$, $M_f = 278$, $A_s = 291$ and $A_f = 303$ K) are almost coincident with the values determined from the DSC curves. The magnetization curves of the martensite phase at 263 K and the parent phase at 309 K are shown in Fig. 5. The martenste phase shows typical magnetization curve of the ferromagnetism, while that of the parent phase is likely the paramagnetic. It is confirmed that the parent phase dose not show spontaneous magnetization from the Arrott plots for the data in Fig. 5, namely, the parent phase is the paramagnetism. These results mean that the magnetic transition is caused by the martensitic transformation from the paramagnetic parent phase to the ferromagnetic martensite phase in analogy with a $Co_{35}Ni_{35}Al_{30}$ (B2)[9] and $Ni_{54.75}Mn_{20.25}Ga_{25}$ ($L2_1$) Heusler alloys.[20] The saturation magnetization M_s and the high-field susceptibility χ_{hf} of the martensite phase at 263 K are esti-

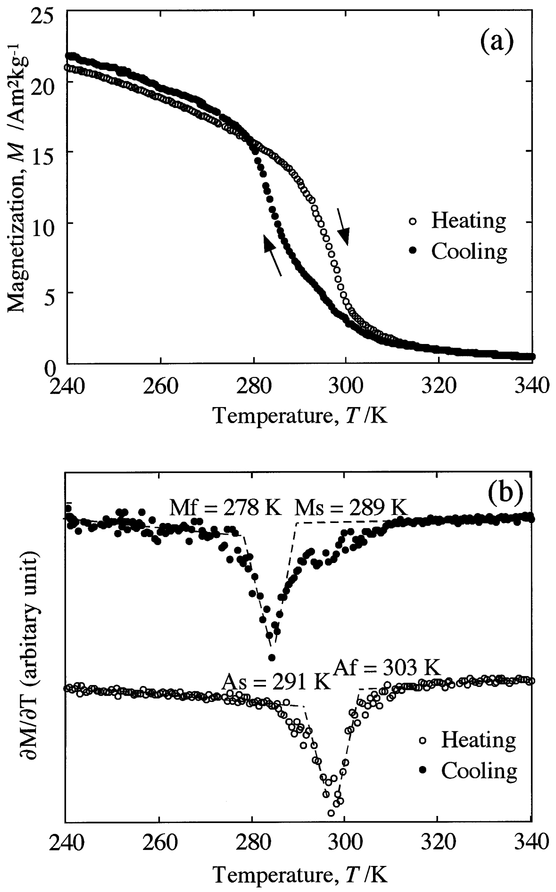

Fig. 4 Temperature dependences of the magnetic properties in a magnetic field of $0.04\,\mathrm{MAm^{-1}}$ for $Ni_{54}Ga_{27}Fe_{19}$ alloy. (a) magnetizations M of heating and cooling processes, (b) temperature derivative of magnetization, $\partial M/\partial T$.

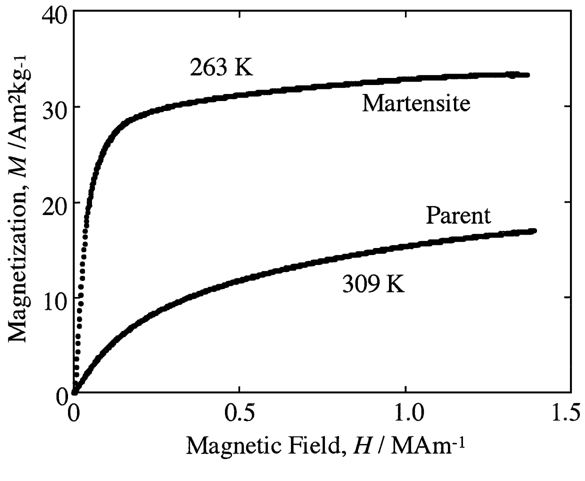

Fig. 5 Magnetization curves of the martensite phase at 263 K and the parent phase at 309 K for $Ni_{54}Ga_{27}Fe_{19}$ alloy.

mated from the law of approach to saturation[21] as $M_s = 29.5\,\mathrm{Am^2/kg}$ and $\chi_{hf} = 3.45 \cdot 10^{-6}\,\mathrm{m^3/kg}$. These values are lager than those of the $Co_{35}Ni_{35}Al_{30}$ alloy in the martensite phase near As temperature evaluated as $M_s = 25.0\,\mathrm{Am^2/kg}$ and $\chi_{hf} = 2.60 \cdot 10^{-6}\,\mathrm{m^3/kg}$ at 233 K.[22] These results suggest that the martensitic transformation in the $Ni_{54}Ga_{27}Fe_{19}$ alloy is expected to be induced by lower magnetic field than that of the $Co_{35}Ni_{35}Al_{30}$ alloy.

4. Conclusion

The martensitic and magnetic transitions of $Ni_{54}Ga_{27}Fe_{19}$ alloy have been investigated. This alloy martensitically transforms from a $L2_1$ parent phase to a 14M martensite phase. The ferromagnetic transition is caused by the martensitic transformation from a paramagnetic parent phase to a ferromagnetic martensite phase. The present Ni–Ga–Fe system is promising as a new ferromagnetic shape memory alloy.

Acknowledgments

The authors appreciate the fruitful discussion with Dr. A. Fujita and Prof. K. Fukamichi, Tohoku University. A part of the present study was supported by the Grant-in-Aids for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

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