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Microstructure and martensitic transformation of Ni–Fe–Ga–Si ferromagnetic shape memory alloys

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ABSTRACT

The effects of the fourth element Si on the martensitic transformation and magnetic properties of Ni–Fe–Ga magnetic shape memory alloys were investigated. A complete thermoelastic martensitic transformation in Ni–Fe–Ga–Si alloys was observed in the temperature range of 218–285 K. The martensitic transformation temperatures of Ni–Fe–Ga alloys are obviously decreased by the substitution of Si for Ga element, that is, the substitution of 1 at.% Si for Ga leads to a decrease of martensitic transformation temperature of about 39.6 K. Moreover, the substitution of Si for Ga leads to a decrease of the saturation magnetic field and the magnetic anisotropy constant K_1 obviously.

1. Introduction

Magnetic shape memory alloys (MSMAs) have received much attention due to their unique potential applications as actuators in microelectromechnical systems [1,2]. In Ni–Mn–Ga alloys, a large magnetic-field-induced strain up to 6% has been reported [3]. However, the brittleness of Ni–Mn–Ga alloys is the main obstacle for practical applications. Recently, Ni–Fe–Ga alloys have been discovered to be a promising actuator material because of its high toughness and being more suitable when used in engineering fields [4–8]. Because the martensitic start temperature (M_s temperature) is very sensitive to the composition, the previous work emphasized on the enhancement of the M_s temperatures by adjusting the alloy compositions. At the same time, alloying with some trace elements is also an effective means to control the M_s temperature. Tsuchiya et al. [9] studied the alloying of Co, Cu, Al, Ge and Sn in Ni–Mn–Ga alloys. Lu et al. [10] compared different Ni–Mn–Ga–(C, Si, Ge) alloys with the ternary one. Söderberg et al. [11] studied the effect of Bi, Pb, Si, Sn and Zn in Ni–Mn–Ga alloys. In their work, the effects of the fourth element on the martensitic transformation behavior, magnetic and mechanical properties have been studied. Recently, Liu et al. [12] found that doping Si into Co–Ni–Ga alloys can improve the magnetocrystalline anisotropy energy and Curie temperature as well. As for Ni–Fe–Ga alloys, Zheng et al. [5,13] studied alloying Ni–Fe–Ga with Co, Ag, In and Cu. Oikawa et al. investigated the effect of Co on the martensitic transformation and the magnetic properties in Ni–Fe–Ga alloys [14,15]. However, little information about alloying Ni–Fe–Ga system with other trace element such as Si is available to date. In this paper, the role of Si on the microstructure, crystal structure, martensitic transformation and magnetic properties of Ni–Fe–Ga alloy was investigated systematically.

2. Experimental

Polycrystalline samples about 30 g of $Ni_{55.3}Fe_{17.3}Ga_{27.4-x}Si_x$ ($x = 0, 0.5, 1, 2$) alloys were prepared by arc-melting under an argon atmosphere (the purity of the elements is higher than 99.99%). The samples were melted four times in a water cooling copper crucible to ensure homogeneity and then heat treated at 1372 K for 3 h to enhance homogeneity followed by quenching into ice water. The obtained specimens were sealed in vacuum silica tubes, heated to 773 K for 1 h to reduce its residual stress and then cooled slowly to room temperature.

Microstructure observation was carried out using a Neoplot-1 optical microscope. The phase transformation temperatures were measured in a modulated differential scanning calorimeter (MDSC-2910) with heating and cooling rates of ±10 K/min. The chemical composition of the phases was determined by an energy dispersive spectrometer (EDS) using a standard calibration method. Phase identification was performed in X-ray diffraction (D/max 2550 V XRD) with Cu Kα radiation. Samples with a dimension of Ø 3 mm × 5 mm were subjected to the magnetic measurement in a conventional vibration sample magnetometer (VSM).

3. Results and discussion

Fig. 1 shows the optical micrograph of $Ni_{55.3}Fe_{17.3}Ga_{27.4-x}Si_x$ ($x = 0, 0.5, 1, 2$) alloys. It is evident that the addition of Si markedly changes the microstructure of the ternary $Ni_{55.3}Fe_{17.3}Ga_{27.4}$ alloy. The $Ni_{55.3}Fe_{17.3}Ga_{27.4}$ alloy exhibits a typical stripe-like surface relief morphology consisting with the well-accommodated martensitic variants, as shown in Fig. 1(a). This indicates that the thermoelastic martensitic transformation occurs above room temperature. When the content of Si is 0.5 at.%, the alloy completely

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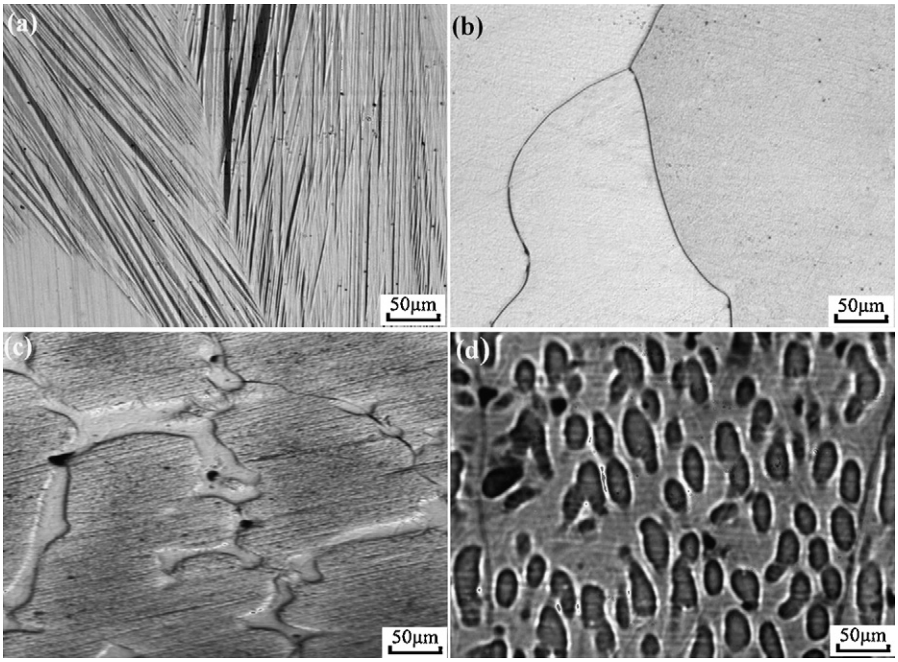

Fig. 1. Optical image of microstructure of $Ni_{55.3}Fe_{17.3}Ga_{27.4}$ (a), $Ni_{55.3}Fe_{17.3}Ga_{26.9}Si_{0.5}$ (b), $Ni_{55.3}Fe_{17.3}Ga_{26.4}Si_1$ (c) and $Ni_{55.3}Fe_{17.3}Ga_{25.4}Si_2$ (d) alloys.

transforms into an austenite phase, as seen in Fig. 1(b). With increasing the content of Si to 1 at.% and 2 at.%, the dendrites originate from a peritectic reaction during solidification, a typical morphology of the two phase structure is shown in Fig. 1(c) and (d). From the XRD patterns as seen in Fig. 2, the dendritic phase is indexed to be the γ phase. The results of EDS analysis indicated that the matrix phase is rich in Ga while the γ interdendritic phase is rich in Ni and Si, as seen in Table 1.

Fig. 2 shows the XRD patterns of the Ni–Fe–Ga–Si alloys at room temperature, where typical martensitic peaks can be seen clearly in Ni–Fe–Ga alloy, and the coexistence of γ and austenite peaks appear in Ni–Fe–Ga–Si alloys. Since the XRD peaks corresponding to the martensite are rather similar to those in $Ni_{55.5}Fe_{17.5}Ga_{27.5}$ alloy [5], we index the martensite structure by a seven-layered (14 M) modulated monoclinic structure.

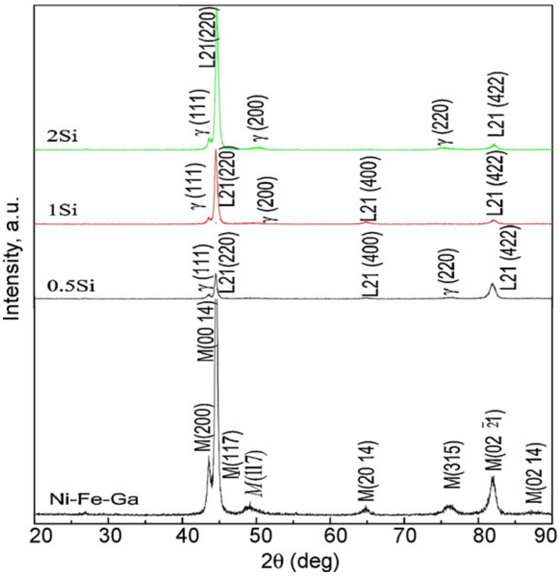

Fig. 2. XRD patterns of the Ni–Fe–Ga–Si alloys.

From an application point of view, M_s temperature above room temperature is important for a FMSMAs besides its magnetization properties. Fig. 3 shows the DSC curves for $Ni_{55.3}Fe_{17.3}Ga_{27.4-x}Si_x$ ($x = 0$, 0.5, 1, 2) alloys. The results show that there is only one endothermic and exothermic peak during heating and cooling process, respectively, indicating that one-step phase transformation appears in Ni–Fe–Ga–Si alloys. The effect of the Si content on the martensitic transformation temperatures of $Ni_{55.3}Fe_{17.3}Ga_{27.4-x}Si_x$ ($x = 0$, 0.5, 1, 2) alloys is shown in Fig. 4. It is evident that phase transformation temperatures of the alloys decrease remarkably with the increase of the Si content. It has been generally accepted that a change of the electron concentration (e/a) significantly affects M_s in Ni–Mn–Ga alloys [16]. In the present case, the dendrites γ phase is responsible for the decrease of the transformation temperature. The γ phase is considered to be a Ni–Fe–Ga alloy which is rich in Ni, Fe and poor in Ga, so the forming of the γ phase makes the content of Ga slightly increased in matrix, as seen in the Table 1, which means that decreased the average electron concentration e/a of the matrix. According to the date obtained from the DSC curve, the thermal hysteresis of $Ni_{55.3}Fe_{17.3}Ga_{27.3}$ is about 12 K while that of $Ni_{55.3}Fe_{17.3}Ga_{25.3}Si_1$ is about 7.5 K, which implied that the thermal hysteresis is obviously decreased due to Si doping into Ni–Fe–Ga alloy. That shows the decrease of the thermal hysteresis due to the addition of Si reduces the friction loss of the phase boundary sharply during martensitic transformation, which benefits a two-way shape memory performance of materials [17].

Fig. 5 displays the magnetization curves of $Ni_{55.3}Fe_{17.3}Ga_{27.4-x}Si_x$ ($x = 0$, 0.5, 1, 2) alloys at room temperature. The saturation magnetization (M_s) and the magnetic anisotropy constant K_1, which have been recognized as favorable factors to a magnetic-field-induced

Table 1
Nominal compositions of different regions in $Ni_{55.3}Fe_{17.3}Ga_{27.3}$ and $Ni_{55.3}Fe_{17.3}Ga_{25.3}Si_2$ alloys obtained by EDS (at.%).

Nominal composition	Area	Ni	Fe	Ga	Si
$Ni_{55.3}Fe_{17.3}Ga_{27.3}$	Martensitic phase	55.21	17.58	27.21	0
$Ni_{55.3}Fe_{17.3}Ga_{25.3}Si_2$	Matrix	54.31	15.52	28.35	1.82
	Dentrites gamma phase	61.58	24.11	10.53	3.78

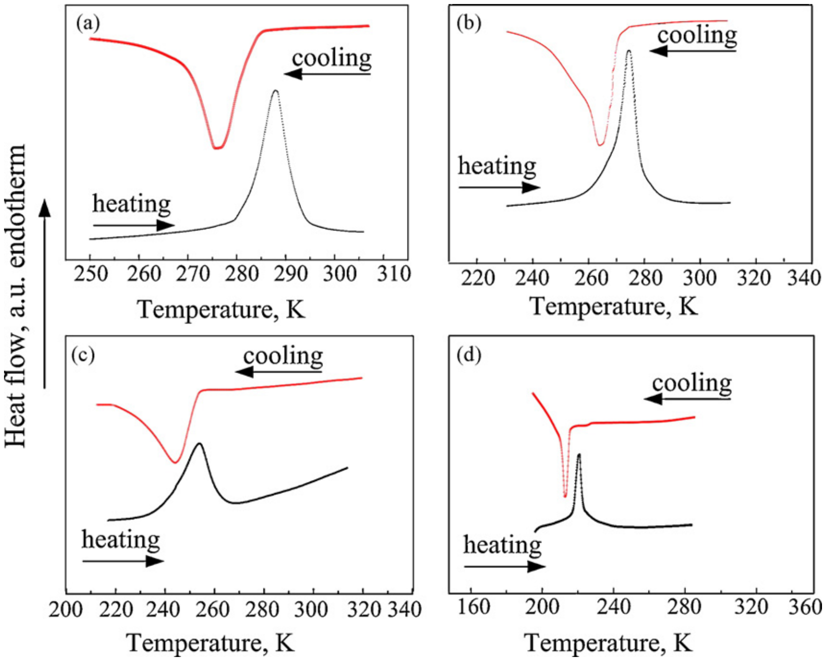

Fig. 3. DSC curves of $Ni_{55.3}Fe_{17.3}Ga_{27.4}$ (a), $Ni_{55.3}Fe_{17.3}Ga_{26.9}Si_{0.5}$ (b), $Ni_{55.3}Fe_{17.3}Ga_{26.4}Si_1$ (c) and $Ni_{55.3}Fe_{17.3}Ga_{25.4}Si_2$ (d) alloys.

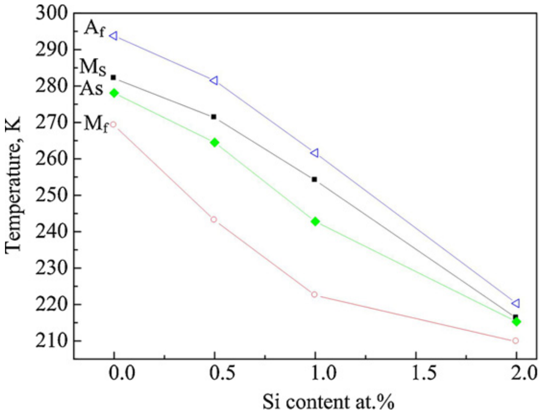

Fig. 4. The effect of Si content on phase transformation temperatures of $Ni_{55.3}Fe_{17.3}Ga_{27.4-x}Si_x$ ($x = 0$, 0.5, 1, 2) alloys.

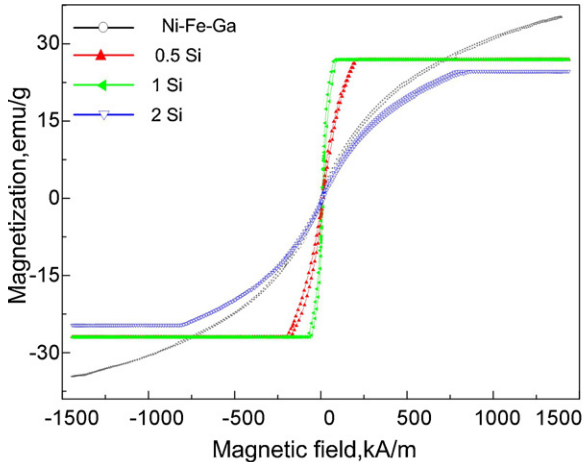

Fig. 5. Magnetization curves of Ni–Fe–Ga–Si alloys at room temperature.

strain, can be estimated by magnetization curves [18]. It is well known that the magnetization of the Ni_2MnGa Heusler alloy is mainly decided by the magnetic exchanges interaction between Mn atoms [19]. The Fe atoms in Ni_2FeGa, occupies the Mn sites of the Ni_2MnGa, play an important role in its magnetic performances. From Fig. 5, one can see that the magnetization curves of Ni–Fe–Ga–Si alloys can be more easily magnetized than that in Ni–Fe–Ga alloys. This is due to the different magnetic anisotropies between martensite and austenite. The saturation magnetization (M_s) and magnetic anisotropy constant K_1 of the austenitic phase calculated by the law of approach to saturation from the magnetization curves are 26.25 emu/g and 2.104×10^4 erg/cm^3, while the saturation magnetization of the martensitic phase is more than 30 emu/g and K_1 of the martensitic phase is 1.171×10^6 erg/cm^3, respectively. From the date of the M_s and K_1, one can clear that Ni–Fe–Ga–Si alloys can be more easily magnetized than Ni–Fe–Ga alloys. Moreover, the study of Liu et al. [20] also confirmed that the magnetization is hard to saturate for martensite while easily for austenite. From Figs. 1 and 2, it is clear that the microstructure of $Ni_{55.3}Fe_{17.3}Ga_{27.4}$ is martensitic phase, while that of $Ni_{55.3}Fe_{17.3}Ga_{27.4-x}Si_x$ alloys are austenite and the γ phase, respectively. So Ni–Fe–Ga–Si alloys are easily saturated in the low magnetic field but Ni–Fe–Ga alloy is hard to be saturated. It cannot get saturated for Ni–Fe–Ga alloy even in magnetic field approaching 1500 kA/m.

4. Conclusions

The microstructure, crystal structure, martensitic transformation and magnetic properties of $Ni_{55.3}Fe_{17.3}Ga_{27.4-x}Si_x$ ($x = 0$, 0.5, 1, 2) alloys were studied. The results show that the martensitic transformation temperatures decreased with increasing of the Si content in Ni–Fe–Ga alloys mainly due to the presence of the dendritic γ phase. The thermal hysteresis of Ni–Fe–Ga alloys also decreased with the increasing of the Si content. The substitution of Si for Ga leads to a reduction of the saturated magnetic field because of the formation of the austenite, which gives a new idea to explore low magnetic field ferromagnetic shape memory alloy.

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