# The effect of Si content on the martensitic transformation temperature of $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$* alloys

Shen Hua-Hai(申华海)[a], Yu Hua-Jun(余华军)[b], Fu Hao(付 浩)[a], Guo Yuan-Jun(郭袁俊)[a], Fu Yong-Qing(傅永庆)[c], and Zu Xiao-Tao(祖小涛)[a]†

[a] *Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu* 610054, *China*
[b] *The College of Physics and Electronic Information, Gannan Normal University, Ganzhou* 314000, *Jiangxi Province, China*
[c] *School of Engineering and Physical Sciences, Heriot Watt University, Edinburgh, EH14 4AS, UK*

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This paper investigates the effects of substitution of Si for Ga on the martensitic transformation behaviours in Ni–Fe–Ga alloys by using optical metallographic microscope and differential scanning calorimetry (DSC) methods. The structure type of $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ alloys is determined by x-ray diffraction (XRD), and the XRD patterns show the microstructure of Ni–Fe–Ga–Si alloys transformed from body-centred tetragonal martensite (with Si content $x = 0$) to body-centred cubic austenite (with $x = 2$) at room temperature. The martensitic transformation temperatures of the $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ alloys decrease almost linearly with increasing Si content in the Si content range of $x \leq 3$. Thermal treatment also plays an important role on martensitic transformation temperatures in the Ni–Fe–Ga–Si alloy. The valence electronic concentrations, size factor, $L2_1$ degree of order and strength of parent phase influence the martensitic transformation temperatures of the Ni–Fe–Ga–Si alloys. An understanding of the relationship between martensitic transformation temperatures and Si content will be significant for designing an appropriate Ni–Fe–Ga–Si alloy for a specific application at a given temperature.

**Keywords:** Ni–Fe–Ga alloys, ferromagnetic shape memory alloys, martensitic transformation, thermal treatment

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## 1. Introduction

In recent years, ferromagnetic shape memory alloys (FSMAs) have become an important part of sensor and actuator materials due to their large magnetic-field-induced strain and shape memory effect. To date, several alloy systems have been developed as FSMA candidates, such as Ni–Mn–Ga,[1,2] Ni–Mn–Al,[3] Fe–Pd,[4] and Co–Ni–Ga.[5] The ternary alloy system Ni–Fe–Ga advanced by Oikawa *et al.*[6] exhibits excellent thermoelastic martensitic transformation (MT) and has received extensive attention. The martensitic transformation in these alloys is correlative with a structural transition from a parent phase $B2/L2_1$ heusler structure to modulated layered structures (i.e. five layered, 10 M and seven layered, 14 M). The MT temperatures are critical for the application of these alloys and they are very sensitive to the alloy compositions.[6] Currently, alloying is thought to be an effective way to adjust the MT temperatures and other mechanical and functional properties. The effects of the addition of Co, Fe, Si, Nd, Dy, Gd, Sm and In on the MT of the Ni–Mn–Ga and Co–Ni–Ga alloys have been investigated. Oikawa *et al.*[7] reported that the MT temperatures increased with the substitution of Fe atoms with Co in $Ni_{51}Fe_{22-x}Ga_{27}Co_x$ alloys, while the Curie temperatures decreased slowly with increasing Co content. Zheng *et al.*[8] reported that substitution of 4.5 at% Ga with Co in a $Ni_{56.5}Fe_{19.0}Ga_{24.5}$ alloy leads to an increase in the $M_s$ temperature from 300 K to 388 K, whereas the $M_s$ temperature decreases from 300.54 K to 299.30 K with substitution of 1 at% Ag for Ni. The addition of Si will significantly influence the microstructure and the MT behaviours of Ni–Fe–Ga alloys. Yu *et al.*[9] investigated the changes in MT characteristics due to the substitution of Ge in Ni–Fe–Ga, and found that MT temperatures decrease linearly with increasing Ge con-

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†Corresponding author. E-mail: xtzu@uestc.edu.cn

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tent. However, as far as we know, there is no report on the substitution of Si in Ni–Fe–Ga alloys. In the present work, the effects of the addition of Si on the phase structure and the MT temperatures of the polycrystalline $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ FSMAs were investigated. Heat treatments were performed at 200 °C–500 °C for 0.5 hours to study the relationship between the MT temperature and the annealing temperature.

## 2. Experiment

A series of polycrystalline alloys with a nominal composition of $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ ($x$ = 0, 0.5, 1, 2, 3) with a weight of $\sim$ 10 g were prepared by using a suction-casting method. These alloys were fabricated by melting four times in a non-consumed vacuum arc furnace under an argon atmosphere using appropriate quantities of Ni (99.99% purity), Fe (99.99% purity), Ga (99.99% purity) and Si (99.99% purity). The obtained ingots were re-melted and suction-cast into a cylindrical copper mold set at the bottom of the furnace to prepare a rod with a diameter of $\sim$ 3 mm. The samples subjected to the investigation were cut from the rod ingots with a low speed diamond saw machine.

The microstructures of the as-cast alloy foils were observed by an optical metallography microscope (Neophoto-I) after the samples were polished and etched with a solution of 10-g $FeCl_3{\cdot}6H_2O$ + 25-ml HCl + 75-ml $H_2O$. The transformation temperature measurements were performed by a differential scanning calorimeter (DSC131, Setaram Company, France) with a scanning rate of 15 $K \cdot min^{-1}$ in nitrogen atmosphere. The phase structures were investigated by using the x-ray diffraction (XRD) technique performed with a DX-2500 diffractometer (Dandong, China).

## 3. Results and discussion

The microstructures of $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ ($x$ = 0, 1, 2) alloys at room temperature observed by using the optical metallography technique are shown in Fig. 1. As shown in Figs. 1(a) and 1(b), the plate-like martensites can be observed in ternary $Ni_{55.5}Fe_{18}Ga_{26.5}$ and quaternary $Ni_{55.5}Fe_{18}Ga_{25.5}Si_1$ alloys. When the substitution of Ga with Si was increased to 2 at%, the plate-like martensite could not be observed, and the microstructure showed the characteristics of the high-temperature austenite phase confirmed by the following XRD pattern (in Fig. 2(c)). The above results indicated that the addition of Si element into Ni–Fe–Ga alloys will decrease the MT temperature of the alloys, and induce the change in microstructure from the low-temperature martensite phase to the high-temperature austenite phase.

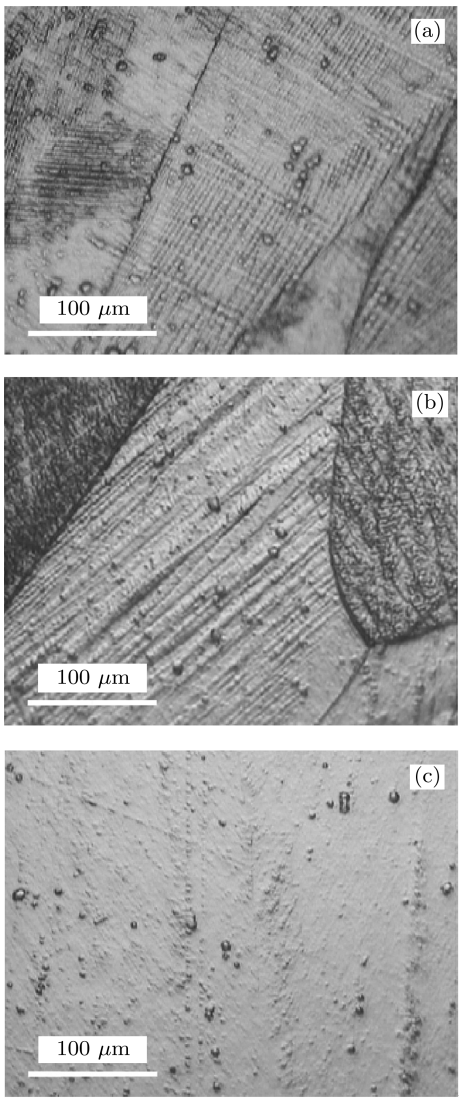



**Fig. 1.** The optical microscope photograph of $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ alloys at room temperature: (a) $x = 0$; (b) $x = 1$; (c) $x = 2$.

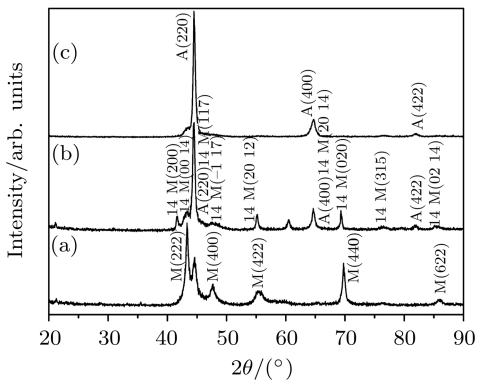



**Fig. 2.** The XRD diffraction pattern of $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ alloys at room temperature: (a) $x = 0$; (b) $x = 1$; (c) $x = 2$.

Figure 2 shows the XRD patterns of the alloys $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ ($x$ = 0, 1, 2) at room temperature. The peaks of the $Ni_{55.5}Fe_{18}Ga_{26.5}$ polycrystalline alloy can be indexed as body-centred tetragonal martensite with the lattice constant of $a = b =$ 0.7638 nm, $c$ = 0.6594 nm (Fig. 2(a)). The peaks of $Ni_{55.5}Fe_{18}Ga_{25.5}Si_1$ can be indexed as the composite structures of 14-M orthorhombic and body-centred cubic (BCC) austenite (Fig. 2(b)), whereas the peaks of $Ni_{55.5}Fe_{18}Ga_{24.5}Si_2$ can be indexed as a single body-centred cubic structure with a lattice constant of $a = b = c = 0.5756$ nm (Fig. 2(c)). The XRD results show that with an increase in Si content, the phase structure of $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ transforms from martensite to austenite at room temperature, which is consistent with the above observation from the optical images.

Figure 3 presents the DSC curves of the alloys $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ ($x$ = 0, 0.5, 1, 2, 3) upon cooling and heating with a scanning rate of 15 $K \cdot min^{-1}$. The results show that there is only one endothermic and exothermic peak during the heating and cooling process, indicating that one-step phase transformation occurs in the $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ alloys. The start and end of the transformation temperatures have been determined by noting the intersection of a baseline and the tangents to each peak. The points $M_s$ and $M_f$ are the start and finish temperatures of the MT, respectively, and points $A_s$ and $A_f$ are those of the reverse phase transformation (as shown in Fig. 3). The dependences of the MT temperatures upon Si content are listed in Table 1. From Fig. 3 and Table 1, it is evident that the transformation temperatures of the alloys decrease remarkably with increasing Si content. For example, $M_s$ decreases from 349.5 K to 231.1 K as $x$ increases from 0 to 3. In addition, thermal hysteresis ($A_f$–$M_s$) of all of the alloys is about 15 K, indicating that adding Si will not change the characteristics of thermoelastic MT.

**Table 1.** Start ($M_s$) and finish ($M_f$) temperatures of MT, start ($A_s$) and finish ($A_f$) temperatures of reverse MT, and the thermal hysteresis $T_h$ ($T_h = A_f - M_s$) of $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ alloys.

| Si content | $A_s$/K | $A_f$/K | $M_s$/K | $M_f$/K | $T_h$/K |
|---|---|---|---|---|---|
| $x = 0$ | 354.4 | 361.6 | 349.5 | 344.4 | 12.1 |
| $x = 0.5$ | 338.0 | 346.0 | 334.4 | 328.3 | 11.6 |
| $x = 1.0$ | 295.6 | 303.4 | 287.9 | 277.5 | 15.5 |
| $x = 2.0$ | 260.8 | 270.0 | 252.4 | 244.1 | 17.6 |
| $x = 3.0$ | 237.7 | 246.9 | 231.1 | 224.0 | 15.8 |

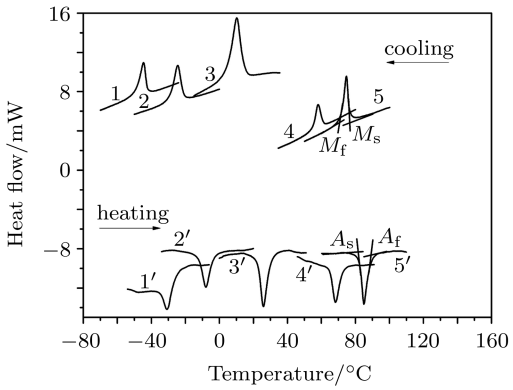



**Fig. 3.** DSC result of $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ alloys upon heating and cooling. In the figure, the groups of numbers mean 1 1′: $Ni_{55.5}Fe_{18}Ga_{23.5}Si_3$; 2 2′: $Ni_{55.5}Fe_{18}Ga_{24.5}Si_2$; 3 3′: $Ni_{55.5}Fe_{18}Ga_{25.5}Si_1$; 4 4′: $Ni_{55.5}Fe_{18}Ga_{26}Si_{0.5}$; 5 5′: $Ni_{55.5}Fe_{18}Ga_{26.5}$.

The MT temperatures as a function of valence electron concentration ($e/a$) of $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ ($x$ = 0, 0.5, 1, 2, 3) alloys are shown in Fig. 4. The tendency is clear that all transformation temperatures decrease with increasing $e/a$ in the series of alloys, and the increasing rate is also consistent with the change in electronic concentration. Here, it is assumed that the number of valence electrons per atom for Ni, Fe, Ga, and Si elements is 10 ($3d^84s^2$), 8 ($3d^64s^2$), 3 ($4s^24p^1$), and 4 ($3s^2p^2$), respectively.

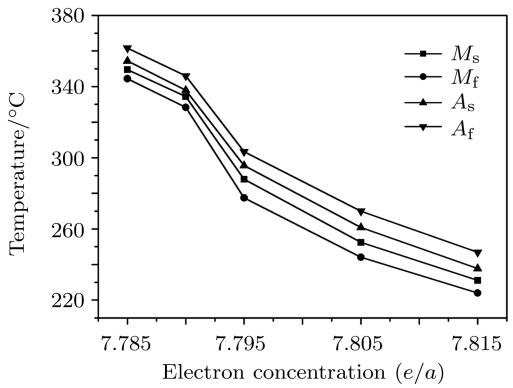



**Fig. 4.** The relationship of the transformation temperature and the valence electron concentration of alloys $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$.

It has generally been accepted that the changes in $e/a$ and the size factor significantly influence the temperatures of MT in Ni–Mn–Ga and Ni–Fe–Ga alloys.[10,11] Jin *et al.*[12] reported that the relationship between MT temperature and $e/a$ can be described by using the equation $T_{mart} = 702.5(e/a)$–5067 K, indicating that the MT temperature increases with increasing $e/a$. In addition, the size factor plays a vital role in the MT temperatures in the alloys and it was observed in the $Ni_2MnGa_xIn_{1-x}$ system,[13] where the

decrease in the unit-cell volumes results in an increase in MT temperature with small atom Ga substituting the large atom In. The atomic radii for Ni, Fe, Ga, and Si are 0.125, 0.126, 0.141, and 0.111 nm,[14] respectively. A shrinkage of the unit-cell volume is expected due to smaller atom Si substitution for Ga in the Ni–Fe–Ga–Si alloys. However, the MT temperatures decrease with the increase in Si content, i.e. the decrease in the unit-cell volume, which is contrary to reports in Ref. [13]. From the above discussions, a comparison of the critical MT temperatures of the $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ ($x$ = 0, 0.5, 1, 2, 3) alloys, however, does not exactly follow the critical values of the classical $e/a$ and the size factor, which were also reported by Chen *et al.*,[15] acquired similar consequences with this study when Mn was substituted with Fe in Ni–Mn–Ga alloys.

The mechanism of the effect of Si substituting for Ga on the transformation temperatures can be understood by using ordering degree and strength of the parent phase. Wu *et al.*[16] investigated the effect of the addition of a fourth element on the MT temperatures of a Cu–Zn–Al alloy, and found that the MT temperatures increased with increasing ordering degree of the parent phase. It is known that the Ni–Fe–Ga alloy system is an ordered Heusler-type intermetallic compound with $L2_1$ structure, and the structure of the martensite changes from the BCC $L2_1$ type through the diffusionless MT. The addition of Si decreases the ordering degree of the parent phase and results in a decrease in the MT temperatures in the $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ alloys. In addition, crystallographic investigation of the MTs can be explained by the phenomenological crystallographic theory, indicating that lattice invariant shear plays an important role in the MT.[17] The shear energy is closely related to the strength of the parent phase. With an increase in the strength of the parent phase, the shear energy increases, thus more driving force is needed for the MT, which results in a decrease in the MT temperatures.[18] In the present work, the MT temperatures decrease with increasing strength of the parent phase, which may be explained by the increase in the Si content in $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ ($x$ = 0, 0.5, 1, 2, 3) alloys.

Figure 5 shows the dependence of the annealing temperature on the transformation temperatures of the $Ni_{55.5}Fe_{18}Ga_{26}Si_{0.5}$ alloy. It can be seen that with increasing annealing temperature, the MT temperatures ($M_s$, $M_f$, $A_s$ and $A_f$) deduced from the DSC curves for the annealed sample gradually increase. This fact is consistent with the result of Oikawa *et al.*[19] It is expected that the change in transformation temperatures is mainly attributed to the change in ordering degree of $L2_1$ and the introduction of defects during the suction-casting process. The annealing and subsequent slow cooling provide adequate thermal energy and sufficient time for re-ordering of $L2_1$ improvement in its ordering degree. With elevating annealing temperature, the $L2_1$ ordering degree increases and the phase transformation temperature also increases.

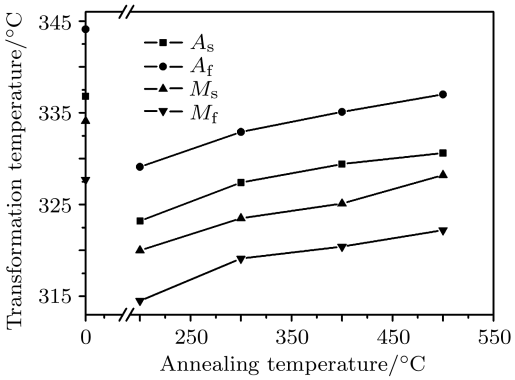



**Fig. 5.** The relationship of transformation temperature and annealing temperature of $Ni_{55.5}Fe_{18}Ga_{26}Si_{0.5}$ alloy.

# 4. Conclusions

Based on the above results and discussions, the conclusions are listed below.

(i) The microstructures of $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ alloys vary with Si content from a body-centred tetragonal martensite for $x = 0$ to a BCC austenite for $x = 2$ at room temperature.

(ii) The $Ni_{55.5}Fe_{18}Ga_{26.5-x}Si_x$ alloys present the typical one-step MT and no extra phase transformation is observed. The transformation temperatures decrease linearly with increasing Si content. Alloying with Si in the NiFeGa alloy is an effective way to tailor the MT temperatures, which is critical in designing the NiFeGa alloy with an appropriate MT temperature for a practical application at different temperatures.

(iii) The change in the MT temperatures of the $Ni_{55.5}Fe_{18}Ga_{26}Si_{0.5}$ alloy, which increases with the annealing temperature, may be attributed to the $L2_1$ ordering degree.

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