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Effect of Ge addition on the martensitic transformation temperatures of Ni–Fe–Ga alloys

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ABSTRACT

A systematical study of substitution of Ge for Ni, Fe, and Ga in the non-stoichiometric NiFeGa alloys was performed in this work. The effect of Ge addition on the structure and martensitic transformation in NiFeGa alloys was investigated by an optical microscope, X-ray diffraction, and differential scanning calorimeters. The results show that the transformation temperatures decrease almost linearly with increasing Ge content in all the three types from higher than 100 down to −90 °C and even lower. The decreases in rate of the martensitic transformation temperatures are different for the three cases. It is large for Ni substituted by Ge, slow for Ga and intermediate for Fe. The determined relationship will be significant for designing a suitable NiFeGa alloy with a required martensitic transformation temperature for application at specific temperature.

1. Introduction

In recent years, the NiFeGa ternary alloy systems have been developed as new member of the ferromagnetic shape memory alloys (FSMAs) [1,2], which are potential alternative to the well-known Ni–Mn–Ga alloys due to their fabricating more easily than Mn-contained alloys because Mn vaporizes at relatively low temperature, as well as their significantly improved ductility [1,3]. Furthermore, NiFeGa alloys exhibit thermoelastic martensitic transformation (MT) upon cooling and heating process. The MT 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) [1]. The MT temperatures are very important for the application of these alloys. It is well known that the MT temperatures are very sensitive to the compositions of this alloy [1,3–5]. The MT temperatures decrease with increasing Fe content at a fixed Ga content. By increasing the Fe content, the MT can occur from either paramagnetic parent phase or ferromagnetic austenite phase to ferromagnetic martensite [1]. Moreover, heat treatment plays a significant role in tailoring the MT temperatures of NiFeGa alloys. Some researchers have reported the aging effects on martensitic and magnetic transitions of NiFeGa alloys [3,6,7].

Presently, alloying is thought to be an effective way to adjust the MT temperatures and the magnetic properties. Guo et al. [8] found that the substitution of Ga element with Fe increased the MT temperatures. However, Liu et al. [9] observed that as the Mn atoms were substituted with Fe, the MT temperature shifts to lower temperature, while the thermal hysteresis of transformation and the Curie temperature are increased. The effect of Bi, Pb, Sn, Zn, Si, In, Co, and Cu on the MT of NiMnGa alloys has been reported [10–12]. Tsuchiya et al. [13] and Gao et al. [14,15] doped Ni–Mn–Ga alloys with rare-earth elements (Nd, Sm, Tb, Dy, and Gd) and found that the addition of rare earth significantly influenced the MT behaviors of the alloys. Imano et al. [16] reported that the MT temperatures decreased with the substitution of Ni atoms with Co in Ni–Fe–Ga alloys, while the Curie temperatures increased with increasing Co content. However, Zheng et al. [17] reported that substitution of 4.5 at.% Ga with Co in Ni56.5Fe19.0Ga24.5 alloy leads to an increase of the M_s temperature from 300.54 to 388.24 K. Furthermore, it is suggested that alloying with In is an effective way to change the microstructure and the MT temperatures of Ni–Fe–Ga alloys [18]. The addition of Ge will greatly influence the microstructure, the MT behaviors and the magnetic properties of Ni–Fe–Ga alloys. However, there is no report on the substitution of Ge in Ni–Fe–Ga alloys up to date. In the present work, a systematic study of Ge substitution for Ni, Fe, and Ga was performed to characterize the effect of the addition of Ge on the microstructure and the MT temperatures of polycrystalline $Ni_{56.5}Fe_{17}Ga_{26.5}$ shape memory alloy.

2. Experimental

Three types of alloys with the nominal composition of $Ni_{56.5-x}Fe_{17}Ga_{26.5}Ge_x$ ($x = 0, 0.5, 1, 2$), $Ni_{56.5}Fe_{17-y}Ga_{26.5}Ge_y$ ($y = 0$,

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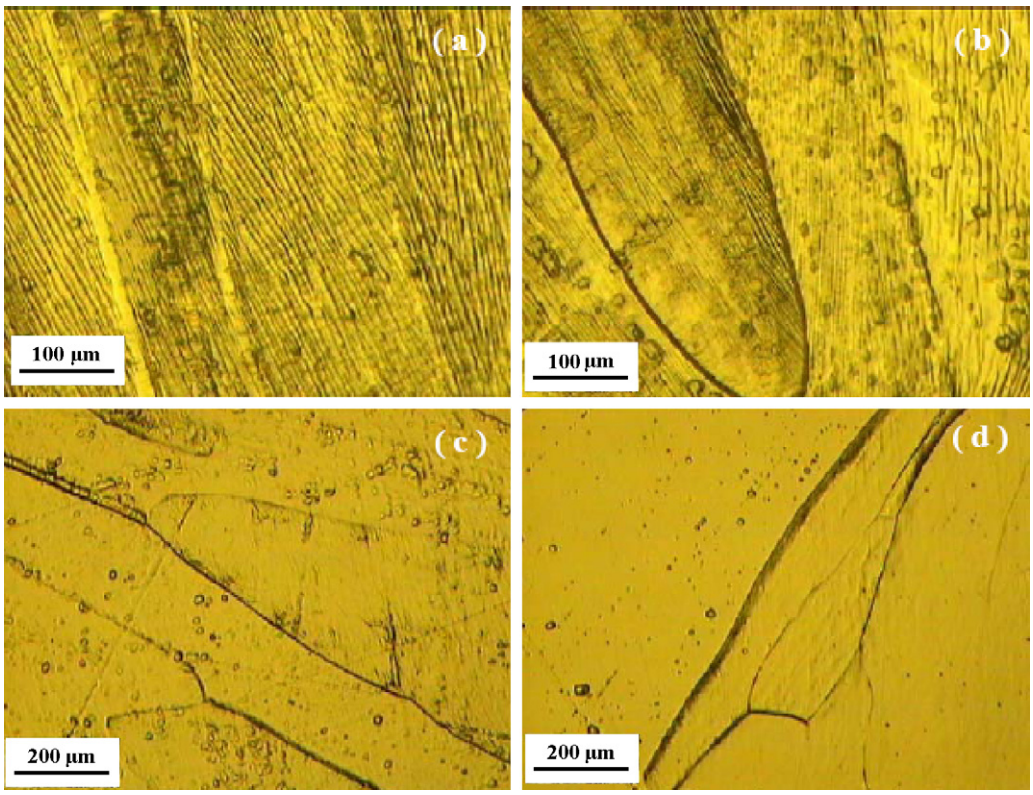

Fig. 1. Optical microscope photographs of $Ni_{56.5-x}Fe_{17}Ga_{26.5}Ge_x$ $x = 0$ (a), $x = 0.5$ (b), $x = 1.0$ (c) and $x = 2.0$ (d) alloys at room temperature.

0.5, 1, 2), and $Ni_{56.5}Fe_{17}Ga_{26.5-z}Ge_z$ ($z = 0$, 1, 2, 3) with weight of ~10 g were prepared using a suck-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 Ge (99.999% purity). The obtained button ingots were re-melted and suction-cast into a cylindrical copper mold set at the bottom furnace to prepare a rod with diameter of ~3 mm.

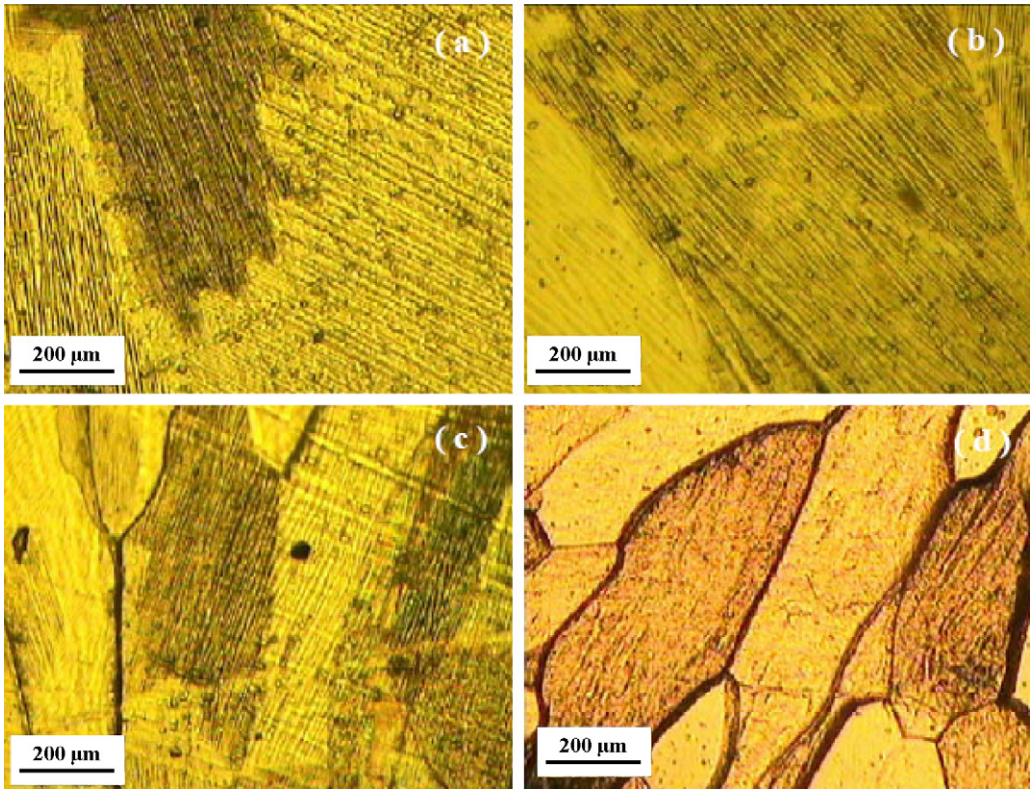

Fig. 2. Optical microscope photographs of $Ni_{56.5}Fe_{17}$ $Ga_{26.5-z}Ge_z$ $z = 1.0$ (a), $z = 2.0$ (b), $z = 3.0$ (c) and $z = 5.0$ (d) alloys at room temperature.

The microstructures of the as-cast alloys foils (extracted from the bottom of the cast rod) were investigated using an optical metallography technique after the samples were polished and etched with the solution of 10 g $FeCl_3 \cdot 6H_2O$ + 25 ml HCl + 75 ml water. The crystal structure at room temperature was confirmed by the X-ray diffraction (XRD) study using a DX-2500 diffractometer (Dandong, China) with Cu Kα radiation. The transformation temperatures were determined by differential scanning calorimeter (DSC131, Setaram Company, France) with heating and cooling rate of 15 K min^{-1} under nitrogen atmosphere.

3. Results and discussion

The microstructures of $Ni_{56.5-x}Fe_{17}Ga_{26.5}Ge_x$ (x = 0, 0.5, 1, 2) and $Ni_{56.5}Fe_{17}Ga_{26.5-z}Ge_z$ (z = 1, 2, 3,5) alloys at room temperature observed using the optical metallography technique were shown in Figs. 1 and 2, respectively. It can be seen from these figures that the microstructure of $Ni_{56.5}Fe_{17}Ga_{26.5}$ show different characteristic with the addition of element Ge. As shown in Fig. 1(a) and (b), the plate-like martensites can be observed in ternary $Ni_{56.5}Fe_{17}Ga_{26.5}$ and quaternary $Ni_{56}Fe_{17}Ga_{26.5}Ge_{0.5}$ alloys. While with the substitution of Ni with Ge was increased to 1 at.%, the plate-like martensites could not be observed, instead the microstructure showed the character of an austenite phase (in Fig. 1(c)). The microstructure of $Ni_{54.5}Fe_{17}Ga_{26.5}Ge_2$ alloy was also single-phase, showing the character of austenite phase (Fig. 1(d)). From Fig. 2(a)–(c), we can see that the pure plate-like martensites were monitored at z = 1, 2 and 3. However, when z of $Ni_{56.5}Fe_{17}$ $Ga_{26.5-z}$ alloys increased to 5, the microstructure showed single-phase structure, the austenite. The above results indicated that the addition of Ge into NiFeGa alloys will induce the decrease of the transformation temperature.

X-ray diffraction (XRD) patterns of $Ni_{56.5-x}Fe_{17}Ga_{26.5}Ge_x$ (x = 0, 0.5, 1, 2) and $Ni_{56.5}Fe_{17}Ga_{26.5-z}Ge_z$ (z = 0, 1, 2, 3, 5) alloys at room temperature are shown in Fig. 3. All reflections were indexed with the martensite structure or austenite structure, and no other phase was monitored by XRD analysis. As shown in Fig. 3(a) the non-stoichiometric $Ni_{56.5}Fe_{17}Ga_{26.5}$ alloy crystallized in the martensite structure. With the increase of Ge substitution for Ni, the crystal structure transformation was found from martensite to austenite at room temperature. With the substitution of 1 and 2 at.% Ni atoms with Ge atoms, the quaternary alloys crystallized in the bcc structure, the austenite. From Fig. 3(b), it can be seen that the martensitic structure was monitored with 1–3 at.% Ge substitution for Ga, and pure bcc austenite was obtained with increasing the content of Ge to 5 at.%. The XRD results show that with the increase of Ge substitution for Ni and Ga, the phase structure of $Ni_{56.5}Fe_{17}Ga_{26.5}$ transformed martensite structure to austensite at room temperature, which is consistent with the above observation of the optical images.

DSC measurements were performed in order to quantitatively investigate the MT temperatures of the three types of alloys, i.e. $Ni_{56.5-x}Fe_{17}Ga_{26.5}Ge_x$, $Ni_{56.5}Fe_{17-y}Ga_{26.5}Ge_y$, and $Ni_{56.5}Fe_{17}Ga_{26.5-z}Ge_z$. Fig. 4 shows the typical DSC curves of $Ni_{56.5}Fe_{17-y}Ga_{26.5}Ge_y$ alloys upon cooling and heating with a scanning rate of 15 K min^{-1}. From these curves, the only one exothermic peak corresponding to the MT during cooling and an endothermic peak corresponding to the reverse transformation during heating can be clearly seen, indicating that one-step phase transformation occurs in $Ni_{56.5}Fe_{17-y}Ga_{26.5}Ge_y$ alloys. This reveals that the quaternary Ni–Fe–Ga–Ge alloys maintain the typical one-step thermoelastic martensitic transformation of the ternary $Ni_{56.5}Fe_{17}$ $Ga_{26.5}$ alloy. The MT starting temperature M_s and finishing temperature M_f, during cooling, the reverse transformation starting temperature A_s and finishing temperature A_f, during heating, were determined by noting the intersection of a baseline and the tangents

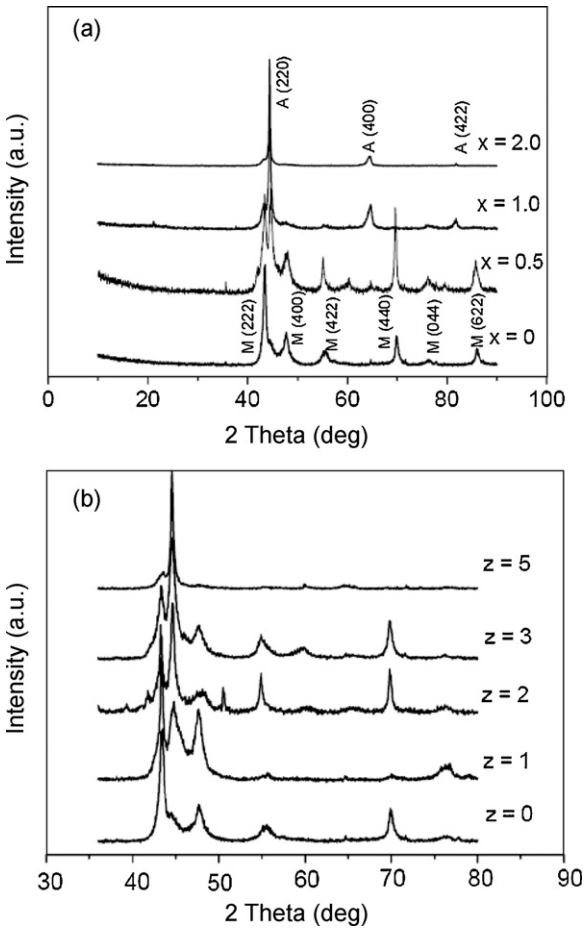

Fig. 3. XRD diffraction pattern of $Ni_{56.5-x}Fe_{17}Ga_{26.5}Ge_x$ (a) and $Ni_{56.5}Fe_{17}$ $Ga_{26.5-z}Ge_z$ (b) alloys at room temperature.

to each peak. The Ge content dependences of the MT temperatures for three series are listed in Table 1. From Table 1, it can be seen that the MT starting temperatures M_s decreases from 108.9 to −94.7 °C as x was increased from 0 to 2; from 86.6 to −17.1 °C as y was increased from 0.5 to 2; and from 89.7 to 2.8 °C as z was increased from 1 to 5. A near linear decrease of the MT temperatures was observed for all the three series of alloys. The DSC results also match well with those of XRD and optical microscope observation for Ge substitution for Ni, Fe, and Ga. Though the MT temperatures

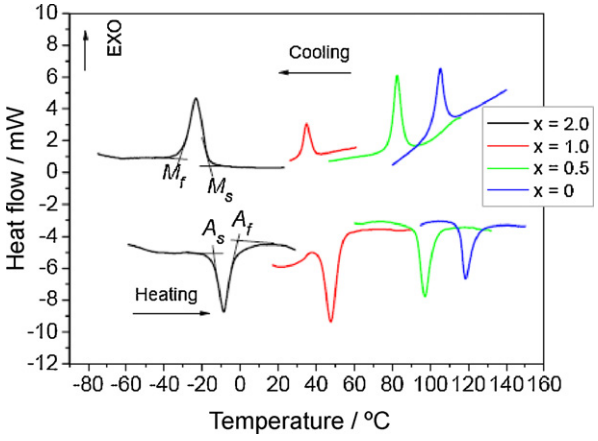

Fig. 4. DSC result of $Ni_{56.5}Fe_{17-y}Ga_{26.5}Ge_y$ (y = 0, 0.5, 1.0, 2.0) alloys upon heating and cooling.

Table 1
the transformation temperatures and valence electronic concentrations of $Ni_{56.5-x}Fe_{17}Ga_{26.5}Ge_x$, $Ni_{56.5}Fe_{17-y}Ga_{26.5}Ge_y$, and $Ni_{56.5}Fe_{17}Ga_{26.5-z}Ge_z$ alloys.

Ge content	e/a	A_s (°C)	A_f (°C)	M_s (°C)	M_l (°C)
0	7.805	115.3	124.5	108.9	101.1
$x=0.5$	7.775	56.5	64.3	51.5	39.3
$x=1.0$	7.745	−7.3	2.9	−10.6	−19.8
$x=2.0$	7.685	−90.3	−81.2	−94.7	−99.9
$y=0.5$	7.795	92.9	102.4	86.6	79.3
$y=1.0$	7.765	42.1	52.9	38.5	31.9
$y=2.0$	7.725	−14.2	−3.5	−17.1	−29.9
$z=1.0$	7.815	101.4	105.3	89.7	81.2
$z=2.0$	7.825	83.7	87.7	74.2	65.1
$z=3.0$	7.835	62.9	66.8	54.4	46.3
$z=5.0$	7.855	12.4	16.3	2.8	−6.7

decrease monotonously with the increase of Ge content in all the three types, the decreasing rates are different. An approximately sharp decrease was found in the order of ~101 °C atomic percent for Ge substitution for Ni, while a slow one for Ga in the order of ~21 °C atomic percent, and intermediate for Fe in the order of ~62 °C atomic percent.

The MT temperatures as a function of valence electron concentration (e/a) in the three series alloys were shown in Fig. 5. The tendency is clear that all transformation temperatures increase with increase of e/a in $Ni_{56.5-x}Fe_{17}Ga_{26.5}Ge_x$ and $Ni_{56.5}Fe_{17-y}Ga_{26.5}Ge_y$ alloys, and the increasing rate is also basically consistent with the change of the e/a (as shown in Fig. 5(a) and (b)). It has been generally accepted that a change of the electron concentration e/a significantly influences the temperatures of martensitic transformation in Ni–Mn–Ga [19] and Ni–Fe–Ga alloys [20]. Here, it is assumed that the number of valence electrons per atom for Ni, Fe, Ga and Ge atoms is 10, 8, 3 and 4, respectively. The e/a values decrease from 7.805 to 7.685 for $Ni_{56.5-x}Fe_{17}Ga_{26.5}Ge_x$ alloys and from 7.805 to 7.725 for $Ni_{56.5}Fe_{17-y}Ga_{26.5}Ge_y$ alloys. Therefore, this principle, that the MT temperatures increase with the increase of e/a, which is used for the description of the MT temperatures vs. e/a in ternary Ni–Mn–Ga and Ni–Fe–Ga alloys, can be applied to the case of the quaternary $Ni_{56.5-x}Fe_{17}Ga_{26.5}Ge_x$ ($x=0$, 0.5, 1, 2) and $Ni_{56.5}Fe_{17-y}Ga_{26.5}Ge_y$ ($y=0$, 0.5, 1, 2) alloys. In addition, the atom size also plays a vital role influencing on the MT temperatures in the alloys. The size factor was observed in $Ni_2MnGa_xIn_{1-x}$ system [21], where the decrease of the unit-cell volumes results in the increase of MT temperatures by small atom Ga substituting the large atom In. Jiang et al. [22] reported that a fall of the unit-cell volumes obtained for smaller atom Ni substitution for Mn, Ga, and both Mn and Ga led to increase of the transformation temperature. Here, the atomic radius for Ni, Fe, Ga, and Ge is 0.1244, 0.1260, 0.1409 and 0.1366 nm, respectively. A similar increase of the unit-cell volumes would be observed as the bigger Ge atom substitutes for Ni or Fe. A big shrinkage of the unit-cell volumes accompanied with Ge substitution for Ga. For example, the lattice parameters of $Ni_{56.5}Fe_{17}$ $Ga_{26.5}$ alloy with tetragonal structure are $a=b=0.7631$ mn, $c=0.6541$ mn and the volume of the unit-cell is 0.3809 mn^3, and those of orthorhombic structure $Ni_{56.5}Fe_{17}Ga_{25.5}Ge_1$ alloy are $a=0.6333$ mn, $b=0.5642$ mn, $c=0.5447$ mn and that of the unit-cell is 0.1946 mn^3, while those of $Ni_{56.5}Fe_{17}Ga_{21.5}$ alloy with cubic structure are $a=b=c=0.5743$ mn and that of the unit-cell is 0.1894 mn^3. The MT temperatures in $Ni_{56.5-x}Fe_{17}Ga_{26.5}Ge_x$ and $Ni_{56.5}Fe_{17-y}Ga_{26.5}Ge_y$ alloys decrease as the unit-cell volumes of the alloys increase. However in the present work, we obtained contrary finding when the small Ge atom substituted for the large atom Ga in $Ni_{56.5}Fe_{17}Ga_{26.5-z}Ge_z$ (as shown in Fig. 5(c)). Ge substituting for the large atom Ga will lead to decrease of the unit-cell volumes and increase of the e/a. While the MT temperatures decrease with decrease of the unit-cell volumes and increase of the e/a, which is contrary to reports in Refs. [21,22].

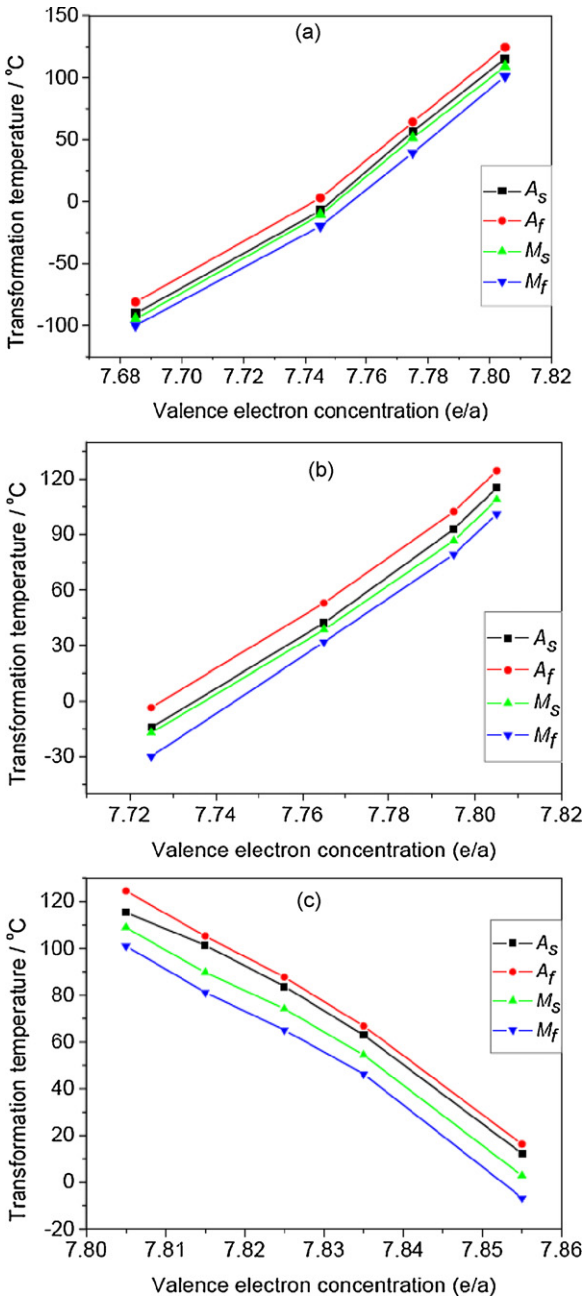

Fig. 5. The phase transformation temperatures as a function of valence electron concentration (e/a) of $Ni_{56.5-x}Fe_{17}Ga_{26.5}Ge_x$ (a), $Ni_{56.5}Fe_{17-y}Ga_{26.5}Ge_y$ (b), and $Ni_{56.5}Fe_{17}Ga_{26.5-z}Ge_z$ (c) alloys.

According to the above results and discussion, it is believed that the mechanism of the effect of Ge substituting for Ga on the transformation temperatures is very complex, which cannot be explained only by the valence electronic concentrations and size factor. Wu et al. [23] investigated the effect of the addition of a fourth element on the MT temperature, and found that the MT temperature increased with increasing degree of ordering of the parent phase. It is known that NiFeGa alloy system is an ordered Heusler type intermetallic compound with $L2_1$ structure [1,3]. The structure of the martensite comes from the bcc $L2_1$ type through the diffusionless MT. The addition of Ge does not change the crystal structure of NiFeGa alloy and the structure of Ge-adding NiFeGa alloys maintains $L2_1$ type as well. However, the increase of the Ge content results in a decrease of the MT temperatures due to decrease in the degree of ordering in $Ni_{56.5}Fe_{17}Ga_{26.5-z}Ge_z$ alloys. Further investigation about the

mechanism of the effect of Ge addition on the MT temperatures is necessary.

4. Conclusions

The martensitic transformation temperatures decrease monotonously with the increase of Ge substitution for Ni, Fe, and Ga in the NiFeGaGe alloys. Alloying with Ge in NiFeGa alloy is an effective way to tailor the MT temperatures, which is significant for designing a NiFeGa alloy with an appropriate MT temperature for practical application at different temperatures. The mechanism of decrease of the MT temperatures with Ge addition is quite complex, and is attributed to no decrease of valence electronic concentration and the unit-cell volumes, but decrease of degree of ordering in the parent phase.

Acknowledgments

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