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Effect of alloying on transformation temperatures and magnetoplasticity in Ni–Mn–Ga alloys

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In this work, the alloying effect ternary Ni–Mn–Ga alloys on the phase transformation temperatures and magnetoplasticity potential has been investigated. Several ternary and quaternary off-stoichiometric compositions of Ni–Mn–Ga alloys and Ni–Mn–Ga–X ones (where X = Si, In, Co, Fe) have been studied. The phase transformation temperatures were determined using differential scanning calorimetry, low-field magnetic susceptibility measurements and tensometry methods. Alloying with the mentioned elements influences considerably the martensitic transformation temperatures. Si and In alloying decreases the martensitic transformation temperatures appreciably, whereas Co increases significantly the ferromagnetic transition temperature T_c. The effect of Fe addition is more complex and depends on which element (Ni, Mn, or Ga) is substituted. The high transformation temperature compositions of the quaternary Ni–Mn–Ga–Fe alloys are found. In a Fe alloyed composition, a strain of 3.5 % has been obtained at 60°C.

В работе исследовано влияние легирования на температуры фазовых превращений и способность к магнитопластичности сплавов Ni–Mn–Ga. Исследовано несколько композиций нестехиометрических сплавов Ni–Mn–Ga и Ni–Mn–Ga–X (где X — Si, In, Co, Fe). Определение температур фазовых превращений проведено при помощи методов низкополевой магнитной восприимчивости, дифференциальной сканирующей калориметрии и метода тензометрии. Легирование выбранными элементами существенно влияет на температуры фазовых превращений. Добавление Si- и In приводит к значительному снижению температур мартенситных превращений. Легирование Co приводит к существенному повышению температуры ферромагнитного превращения T_c. Влияние легирования железом является сложным и зависит от того, какой элемент Ni, Mn или Ga заменяет железо. Найдены высокотемпературные композиции Ni–Mn–Ga–Fe сплавов. В одном из легированных железом сплавов получено 3,5 % деформации под действием магнитного поля при температуре 60°C.

Ternary Ni–Mn–Ga alloys [1–4 and many others] attract a high interest during last years due to the large magnetoelasticity and the magnetic shape memory effect discovered in some compositions of these alloys having the ferromagnetic martensite 5M and 7M modulated crystal lattice (see, e.g., [5–7]). Good prospects for applications such as magnetic and magneto-mechanical actuators and sensors have initiated the search of new alloys with ferromagnetic martensites which are deformed by the magnetic field. The main goal of the alloying Ni–Mn–Ga compounds is primarily to find new ferromagnetic martensitic compositions showing the magnetic shape memory (MSM). Also, there have been attempts to increase the MSM service temperatures of these alloys. However, the information available of the quaternary Ni–Mn–Ga–X alloys is still rather limited [8–17]. Kokorin et al. [8] found out that the substitution In atoms for Ga results in increased lattice parameters, and this causes a lowered Curie point (T_C). Effect of the size factor was observed in $Ni_2MnGa_xIn_{1-x}$ system [8]. Authors have shown that the smaller unit-cell volume results in an increase of martensitic transformation temperature, i.e. in cases where Ga is not substituted by the larger In atom. However, Liu et al. [9] observed that when Fe having smaller ion diameter have substituted for Mn ones, the crystal lattice parameters decrease, but now the martensitic transformation temperature is decreased, the thermal hysteresis increased and the Curie point raised. In [10], Khovailo et al. controlled the Curie temperature by In, V, Co, or Fe alloying, and in [11] the influence of Fe and Co on the phase transformations was studied in more detail. Effect of Fe alloying is also studied in detail in [12]. The study [13] was carried out with a Ni-rich off-stoihiometric Ni–Mn–Ga compound alloyed with Si, C or Ge. Also, in [14] the changes in transformation temperatures were observed with Co, Cu, Al, Sn, and Ge alloying, that work was continued later with rare earth element alloying (Nd, Sm, Tb) in [15]. The effects of selected alloying with Bi, Pb, Sn, Zn and Si on phase transformation are compared in [16]. Depending on the alloying component, the effects are varied: the lattice volume got smaller with Si, Bi, Pb and Zn, but increased with Sn; transformation temperatures decreased to some extent with Pb and Zn, remarkably with Si while with Sn the effect is negligible; with Bi, the transformation temperatures increased; the Curie point decreases only with Bi, while with other elements, it increases slightly.

An empirical correlation between the electron concentration and stability of $L2_1$ structure was reported to justify the hypothesis where the experimental alloys were not systematically selected [17]. In [4], Ni–Mn–Ga alloying by substitution of Ni for Mn, Ga, or both Mn and Ga were performed to study easily the electron concentration dependence on the martensitic transformation temperatures. Effect of alloying with Fe both on the transformation temperatures crystal structure and the electron concentration was systematically studied in [12] for alloys close to the near-stoichiometric Ni–Mn–Ga compositions.

However, the published results concerning the Ni–Mn–Ga alloying effect on the phase transformation temperatures are still insufficient for making conclusions on trends and interrelations between valence electron density and the phase transformation temperatures. In this work, we present the study data of quaternary Ni–Mn–Ga compositions alloyed with Si, In, Fe, and Co. One part of the work concerns the effect of Co and Fe substitution for Ni while the other part deals with the Si and In substitution for Ga. The magnetoplasticity of new magnetic shape memory quaternary high-temperature alloys was examined.

The alloying elements were selected according to their atomic size: with covalent radius smaller or larger than those of elements being substituted, Ga or Ni, respectively (Table 1). In that way, we have studied three groups of alloys (Tables 2, 3, and 4): (i) ternary Ni–Mn–Ga alloys; (ii) quaternary alloys with Si or In partially substituting for Ga; and (iii) quaternary alloys with Co or Fe partially substituting for Ni or Mn. The quaternary materials were prepared using pure Ni, Mn, Ga and master ternary alloy with addition of the alloying elements. Polycrystalline 20 g ingots of the non-stoichiometric ternary Ni–Mn–Ga alloys and quaternary Ni–Mn–Ga–X (X = Si, In, Fe, Co) compositions were melted in alumina Bridgman crucibles in a TIM-500 induction furnace under Ar-atmosphere. Some ingots were preliminary prepared by arc-melting method with quick cooling on a massive copper plate and then re-melted in the induction furnace. Ingots were annealed at 1273 K for 48 h and thereafter at 1073 K for 72 h in evacuated quartz ampoules. Specimens were then cut using a low-speed diamond saw, wet ground and electropolished at ambient temperature with H_2NO_3 + ethanol electrolyte. Chemical compositions were determined by an energy-dis-

Table 1. Valence electrons (e), atomic radius (R), covalent radius

Element	Atomic radius, Å	Valence electrons, e	Covalent radius, Å
Ni	1.246	10	1.15
Mn	1.35	7	1.17
Ga	1,41 (1.81*)	3	1.26
Si	1.32 (1,46*)	4	1.11
In	1.66 (2*)	3	1.44
Co	1.25	9	1.16
Fe	1.26	8	1.16

Table 2. Ternary alloy compositions and phase transformation temperatures

No.	Ni, at%	Mn, at%	Ga, at%	T_c, °C	M_s, °C	M_f , °C	A_s, °C	A_f, °C
15	47.9	26.1	25.8	87	39.1	38.4	51.7	52.1
13	49.70	28.70	21.60	102	32	29.5	38	41
14	50.47	28.17	21.36	106	38	34	41	47
12	51.4	27.2	21.4	93	78	72	80	86
16	51.4	26.7	21.9	92	48	29	44	56
17	50.8	24	25.2	95	−100	−85	−100	−70

Table 3. Quaternary alloy composition and phase transformation temperatures. Alloying elements added instead of Ga partially

No.	Ni, at%	Mn, at%	Ga, at%	X	X, at%	T_c, °C	M_s, °C	M_f, °C	A_s, °C	A_f, °C
Si1	49.86	28.06	22.07	Si	0.47	100	17	12	20	25
Si2	49.96	28.47	21.56	Si	0.55	100.7	27.6	−10	−3.3	36.3
Si3	50.4	28.8	20.8	Si	1	99.6	25.3	−4.8	2.4	31.6
Si4	49.60	27.70	20.60	Si	2.1	108	−128	−136	−111	−103
In2	48.94	24.75	22.90	In	3.41	84.2	5.6	−17.5	−3.1	16
In4	51.72	28.539	19.745	In	4.24	86.3	−95	<−150	<−150	−69.6

persive spectrometer (EDS) connected to a scanning electron microscope (LEO-SEM) and using the chemical analysis carried out with a fluorescent spectroscope. The Curie point T_C and the martensite transformation temperatures M_s, M_f, A_s, A_f were measured in the temperature range −153 +200°C using the low field ac magnetic susceptibility and the differential scanning calorimeter Linkam 600. The most promising compositions having higher martensitic transformation temperatures were chosen for single crystal growing using Bridgman method. Single crystal specimens were tested for magnetoplastic strain using high-sensitive magnetic dilatometer [18].

Table 2 shows the compositions and transition temperatures of the master ternary Ni–Mn–Ga alloys, while in Table 3, presented are those quaternary alloys in which Si or In partially substitute partially for Ga. Fig. 1 shows some examples of the phase transformation temperature measurements for studied alloys. According to Table 3, increasing Si content (the atomic and covalent radii of Si are smaller than those of Ga) decreases temperatures of martensitic transformation drastically (*Si4*) as compared to those obtained for ternary alloys having a close Ni/Mn-ratio (Table 2, No.9). However, the decrease of the transformation temperature is not so drastic for alloy with increased Ni content (Table 3). Effect of Si

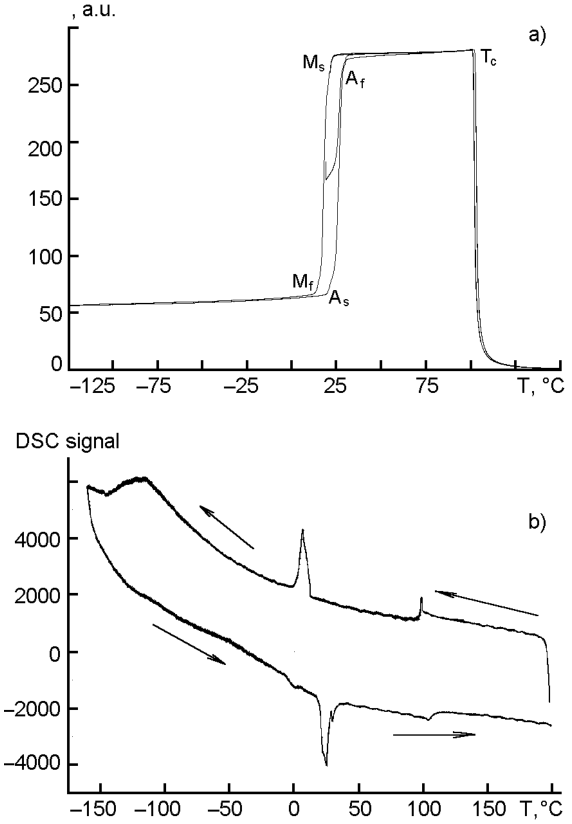

Fig. 1. Some examples of phase transformation temperature measurements: (a) by low field magnetic susceptibility; (b) by using differential scanning calorimeter.

Table 4. The compositions and transition temperatures of the quaternary alloys with Co or Fe

No.	Ni, at%	Mn, at%	Ga, at%	X	X, at%	T_c, °C	M_s, °C	M_f, °C	A_s, °C	A_f, °C
Co2	46.62	25.8	26.57	Co	1.72	125	−7.4	−12	−5.5	−0.1
Co4	43.52	27.9	22.76	Co	5.82	151	−55.5	−60.4	−50.6	−45.8
Co9	50.01	29.06	18.79	Co	2.14	222.8	210.8	224	237	53
F2	49.42	27.62	21.34	Fe	1.8	113	43	39	54	59
F5	47.34	25.86	20.38	Fe	6.42	99.6	12.5	0.5	19.5	29.5
F8	51.33	14.44	26.27	Fe	7.95	115.8/ 95	85.7/ 63.7	78.8/ 51.43	88.2/ 58.48	101/ 77.56
F3	51.8	24.28	24.3	Fe	0.7	102	29	11	21	31
F11	50.9	20.25	23.74	Fe	5.15	128	6.5	2	6	13

addition on the Curie point is insignificant, and to explain this, more detailed crystal structure investigation is needed to clarify especially the Mn–Mn distance. This distance affects heavily the magnetic properties and the Curie temperature, because the magnetic moment is concentrated preferably on Mn atoms in Ni–Mn–Ga based alloys. Addition of In with atomic and covalent radii larger than Ga (Table 1) also decreases the martensitic transformation temperatures (Table 3) as compared to ternary alloy (Table 2).

Table 4 summarises the result for off-stoichiometric quarternary alloys where Co or Fe substitute partially for Ni (Alloys *Co2*, *Co4*, *F2*, *F5*), Mn (Alloy *F3*) or Ga (Alloys *F5*, *Co9*). Substitution of Ni by Co (larger atomic and covalent radis) increases the Curie temperature (Table 3, *Co2*). However, Ni atoms are also partially substituted by the larger Ga atoms. This result does not confirm the possible correlation of the size of alloying element and the Curie temperature [8, 9]. However, when Ga atoms are substituted by Co (much smaller atomic size), the Curie temperature increases drastically (*Co9*), and this is in agreement with observations in [10, 11]. Effect of Fe alloying seems to depend on the element being substituted. If Fe substitutes for Ga, the martensitic transformation temperature decreases (Table 4, Alloy *F3*). If Fe substitutes for Mn (Table 4, *F8*) or partially for Ga (Table 4, *F11*) at slightly increased Ni content, there is a considerable rise in the martensitic transformation temperature. This result does not confirm the conclusion made in [9]. Fe substitution for Ni or Ga shifts the martensitic transformation to the lower temperatures (Table 4, *F5*). However, a small amount of Fe added instead of Ga at higher Mn content increases both the Curie temperature and the martensitic transformation temperatures (Table 4, *F2*). However, when Mn is substituted by the smaller Fe-atoms, the magnetic transition temperature increases (Table 4, Alloys *F8* and *F11*). This is in agreement with [9].

Table 5. Valence electron density per atom (e/a) and ratio of T_c/M_s

No.	Alloy	X	X, at%	T_c/M_s°C
Si1	Si	0.47	1.29	7.6311
Si2	Si	0.55	1.23	7.6577
Si3	Si	1	1.25	7.72
Si4	Si	2.1	2.63	7.601
In2	In	3.41	1.28	7.4158
In4	In	4.24	2.02	7.88928
Co2	Co	1.72	1.5	7.4199
Co4	Co	5.82	1.95	7.5116
Co9	Co	2.14	1.02	7.7915
Fe2	Fe	1.8	1.22	7.6596
Fe5	Fe	6.42	0.94	7.6692
Fe3	Fe	0.7	1.24	7.6646
F8	Fe	7.95	1.08	7.5679
F11	Fe	5.15	1.43	7.6317
12	–	–	1.04	7.686
13	–	–	1.23	7.627
14	–	–	1.22	7.6597
15	–	–	1.15	7.391
16	–	–	1.137072	7.666
17	–	–	2.127168	7.516

It is assumed that the valence electron concentration plays an important role in stabilizing Heusler $L2_1$ structure, defining the magnetic order and affecting the phase transformations and their temperatures in

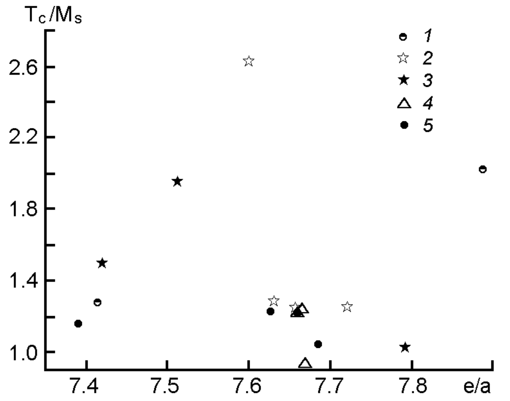

Fig. 2. The T_C/M_s ratio versus e/a in selected Ni–Mn–Ga–X alloys (X = Si, In, Co, Fe).

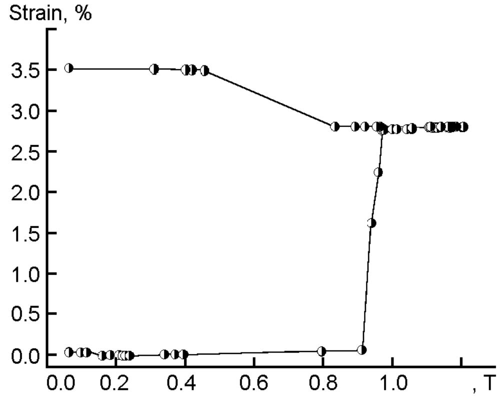

Fig. 3. The magnetic field induced strain in a single crystal of the Alloy *F8* at 60°C.

Ni_2MnGa. Moreover, some authors (see, e.g., [15]) have confirmed a correlation between the increase of the valence electron density and the magnetic and martensitic transformation temperatures for some ternary or quaternary off-stoichimetric Ni–Mn–Ga alloys. We checked the existence of possible T_C/M_s ratio for quaternary alloys studied in this work. These results are shown in Table 5 and Fig. 2. According to these results, there is no clear correlation of T_C/M_s ratio with the electron concentration for any group of the studied quaternary alloys. Any common trend for the applied alloying elements in the studied quaternary compositions seems to be absent.

Some of the alloys were selected for the magnetoplasticity testing, Alloys *F2* and *F3* show the magnetic field induced strain at room temperature and below it. However, the result of magnetoplasticity measurement at 60°C obtained for the Alloy *F8* seems to be the most interesting and promising (Fig. 3). According to the X-ray diffraction pattern,the studied *F8* single crystal has a mixed crystal structure consisting of two martensitic phases: the non-modulated tetragonal and the 7-layered modulated martensite. After the X-ray diffraction study of all three single crystal surfaces, it was confirmed that also the 5-layered modulated type of martensite is present in the structure The co-existence of all three martensite types affects the magnitude of the magnetic field induced strain (2.8–3.5 %) that was found so far only in the modulated types of crystal structures. However, the triggering magnetic field needed for the magnetic field induced strain is rather high, approximately 0.9 T.

Thus, the effect of Si, In, Co and Fe alloying of the off-stoichiometric ternary Ni–Mn–Ga compounds is studied. It is found that alloying with Si and In decreases the martensitic transformation temperatures. Alloying with Co affects heavily the ferromagnetic transformation temperature T_C. However, the effect of Fe addition on the phase transformation is more complex and depends on which element (Ni, Mn or Ga) iron is substitutes for. The high-temperature compositions of quaternary Ni–Mn–Ga–Fe alloys are found. With one of these alloys, a magnetoelastic strain of 3.5 % is obtained at 60°C in a single crystalline sample.

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Вплив легування на температури перетворень та магнетопластичність сплавів Ni–Mn–Ga

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В роботі досліджено вплив легування на температури фазових перетворень та здатність до магнітопластичності сплавів Ni–Mn–Ga. Досліджено декілька композицій нестехіометричніх сплавів Ni–Mn–Ga та Ni–Mn–Ga–X (де X — Si, In, Co, Fe). Визначення температур фазових перетворень проведено за допомогою методів низькопольової магнітної сприятливості, диференціальної скануючої калориметрії та методу тензометрії. Легування означеними елементами суттєво впливає на температури фазових перетворень. Додавання Si та In приводить до значного зниження температур мартенситних перетворень. Легування Co приводить до суттєвого підвищення температури феромагнітного перетворення T_c. Вплив легування залізом є складним і залежить від того, який елемент Ni, Mn чи Ga заміщує залізо. Знайдено високотемпературні композиції Ni–Mn–Ga–Fe сплавів. В одному з легованих залізом сплавів отримано 3,5 % деформації під дією магнітного поля при температурі 60°C.