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Effect of composition on transformation temperatures of Ni–Mn–Ga shape memory alloys

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Abstract

The effect of the composition of Ni–Mn–Ga shape memory alloys (SMAs) on martensitic transformation temperature and enthalpy, Ms and ΔHc, respectively, can be analyzed by linear regression. Experimental results show that the effect of Mn content is relatively small, but Ni and Ga contents have a dramatic effect and their effects are opposed. The Ms temperature and ΔHc of stoichiometric Ni_2MnGa are predicted as 185 K and 1.2 J/g, respectively. The linear relationship between Ms and ΔHc indicates that Ni–Mn–Ga SMAs undergo thermoelastic martensitic transformation.

Keywords: Ni_2MnGa-based intermetallic alloys; Martensitic transformation; Shape memory alloys; Composition effect; Transformation temperature and enthalpy; Linear regression

1. Introduction

Shape memory alloys (SMAs) show the shape memory effect (SME) and pseudoelasticity or superelasticity (PE) which are associated with the thermoelastic martensitic transformation. The unique SME and PE characteristics of SMAs have attracted interest from industries due to their many engineering and medical applications. However, from the viewpoint of applications, the martensitic transformation temperatures of SMAs, such as Ms (the starting temperature of the forward martensitic transformation) and Af (the finishing temperature of the reverse martensitic transformation), are critical factors in industrial design. The Ms temperature is the most important parameter related to the applicable temperature ranges of SMAs' devices. This is the reason why studies of the composition effect on the Ms temperature of SMAs are always interesting topics for SMAs research and development. For binary TiNi SMAs with Ni in the range of 50–51 at.%, the Ms temperature decreases 10–20 K for every 0.1 at.% increase in Ni [1,2]. The Ms temperatures of ternary TiNiX SMAs are affected by the amount of the X element such as X = Cr, Mn, Fe, V, Co, Cu, Pd and Cu [2–5]. For Cu-based SMAs, the composition effect on the Ms temperature has been intensively studied [6–8]. Ms (K) = 2293 − 45Ni (wt.%) − 134Al (wt.%) was reported for Cu–Al–Ni SMAs [6]; Ms (K) = 2221 − 52Zn (wt.%) − 137Al

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(wt.%) for Cu–Zn–Al SMAs with Ms in the range of 173 K – 473 K [7]; and Ms (K) = 1192 − 25.2Al (wt.%) − 73.2Mn (wt.%) for Cu–Al–Mn SMAs [8]. The binary Ni–Al SMAs with Ni being 60.8–69.2 at.% have also been studied and Ms (K) = − 7410 + 124Ni (at.%) was found [9].

The near-stoichiometric Ni_2MnGa SMAs undergo a martensitic transformation and exhibit a ferromagnetic transition near 370 K [10,11]. Chernenko et al. [12] indicated that the Ms temperature of Ni–Mn–Ga based SMAs is highly sensitive to their composition. From the analysis of about 20 specimens, prepared by induction melting, they concluded that at a constant value of Mn content in Ni–Mn–Ga SMAs, Ga addition will lower Ms temperature; at constant Ni concentration, Mn addition will increase Ms temperature; and at constant Ga content, substitution of Ni by Mn will lower Ms temperature. The conclusion of

Table 1
38 kinds of Ni–Mn–Ga SMAs were prepared in this study with their compositions and values of e/a, ΔHc, Ms, Mf, As, Af and Af–Ms

Alloy no.	Ni (at.%)	Mn (at.%)	Ga (at.%)	e/a	ΔHc (J/g)	Ms (K)	Mf (K)	As (K)	Af (K)	Af–Ms (K)
1	50.19	24.71	25.10	7.502	0.33	154.5	146.4	167.4	187.7	33.3
2	50.69	23.07	26.24	7.4708	*	126.9	124.5	130.7	141.0	14.1
3	50.33	23.87	25.80	7.4779	0.41	156.8	121.7	141.1	148.7	8.1
4	50.33	24.38	25.29	7.4983	0.81	157.5	143.5	172.7	184.6	17.1
5	50.49	24.22	25.28	7.5035	1.59	196.5	183.6	208.0	222.7	26.2
6	50.28	24.77	24.96	7.5101	1.25	193.7	186.4	204.4	213.2	19.5
7	50.34	24.80	24.86	7.5158	1.96	203.7	192.2	213.2	223.3	19.6
8	50.36	24.88	24.75	7.5208	1.59	207.8	187.7	215.3	228.3	20.5
9	50.56	24.57	24.87	7.5222	1.12	202.9	185.5	214.1	230.2	27.3
10	50.61	24.84	24.55	7.5363	2.53	231.1	214.8	234.8	251.3	20.2
11	50.41	25.26	24.33	7.5391	2.17	217.3	200.8	225.8	236.9	19.6
12	51.56	23.43	25.02	7.5462	2.24	239.1	222.6	249.7	264.1	25.1
13	51.12	24.30	24.58	7.5504	1.75	224.2	211.6	226.3	240.6	16.4
14	51.93	23.07	25.01	7.5572	2.52	240.1	225.2	251.2	268.3	28.1
15	50.98	24.83	24.19	7.5617	2.44	245.5	234.5	255.7	266.7	21.2
16	50.40	25.85	23.75	7.5620	2.49	237.9	227.6	249.2	256.8	18.9
17	51.27	24.49	24.24	7.5687	3.16	256.5	239.6	265.0	284.6	28.1
18	51.38	24.81	23.81	7.5890	3.25	271.0	260.8	276.9	292.7	21.7
19	51.19	25.20	23.73	7.5943	4.50	285.5	256.0	289.0	307.9	22.4
20	52.84	22.44	24.72	7.5966	4.26	275.7	259.2	287.1	301.1	25.5
21	53.23	21.85	24.92	7.6003	4.71	280.1	268.7	293.0	303.7	23.6
22	50.46	26.74	22.80	7.6078	3.32	265.2	253.7	278.9	286.1	20.9
23	51.71	24.84	23.45	7.6133	3.77	295.9	278.3	296.7	313.4	17.5
24	50.39	27.77	21.84	7.6381	4.33	299.0	288.7	302.7	314.6	15.6
25	52.29	24.59	23.12	7.6439	4.48	310.6	303.4	318.9	323.2	12.6
26	52.14	25.16	22.67	7.6553	5.52	331.4	311.8	337.4	354.6	23.2
27	52.54	24.78	22.68	7.6689	5.94	332.4	314.4	325.7	346.0	13.6
28	52.63	24.73	22.64	7.6733	5.04	327.5	313.0	330.8	347.2	19.7
29	55.78	19.52	24.70	7.6857	6.76	365.2	347.8	375.3	393.2	28.0
30	50.48	28.87	20.65	7.6884	6.36	339.0	309.8	319.9	349.0	10.0
31	50.48	28.87	20.65	7.6884	6.36	339.0	309.8	319.9	349.0	10.0
32	52.84	24.82	22.34	7.6900	7.30	347.3	327.3	340.7	361.3	14.0
33	53.45	24.07	22.48	7.7046	5.87	350.6	328.8	355.1	376.9	26.4
34	53.26	24.68	22.06	7.7100	6.54	373.7	339.7	373.2	394.4	20.6
35	50.37	29.79	19.84	7.7170	7.68	355.2	336.5	353.3	370.5	15.3
36	53.64	24.56	21.82	7.7372	7.89	387.7	353.6	397.3	408.1	20.4
37	53.71	25.27	21.02	7.7705	7.83	431.5	390.2	416.1	450.0	18.6
38	54.15	24.88	20.97	7.7857	8.85	458.3	451.6	474.7	489.5	31.2

*no transformation peak appears.

Ref. [12] is qualitative for understanding the composition effect on the Ms temperature of Ni–Mn–Ga SMAs. However, from the viewpoint of industrial applications, a quantitative composition effect on the Ms temperature of SMAs is necessary. In this study, the quantitative effect of each constituent element on the Ms temperature of Ni–Mn–Ga SMAs is investigated. At the same time, the transformation enthalpy ΔH (J/g) associated with the martensitic transformation versus the composition is also discussed.

2. Experimental procedure

Ingots of Ni–Mn–Ga SMAs weighing about 100 g were prepared by vacuum arc remelting (VAR) from the raw materials of nickel (purity 99.9 wt.%), Mn55-Ni45 mother alloy (in wt.%) and gallium (purity 99.9 wt.%), then homogenizing at 850 °C for 48 h, and finally samples were cut using a low-speed diamond saw for the tests of differential scanning calorimetry (DSC) and electron probe micro-analyzer (EPMA). DSC measurement was conducted by a Dupont 2000 thermal analyzer equipped with a quantitative scanning system 910 DSC cell for controlled heating and cooling in pure N_2 gas. Uncertainty in determining the Ms and ΔHc by DSC was about ± 0.1 K and ± 0.1 J/g, respectively. The compositions of homogenized Ni–Mn–Ga SMAs were determined by EPMA using a JEOL JXA-8600SX model calibrated by specimens whose compositions had been measured by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES), a Jobin Yvon JY38 PLUS model. Uncertainty in determining the concentration of each element by EPMA was about ± 0.3 at.%. Table 1 shows the results of EPMA and DSC tests on 38 kinds of Ni–Mn–Ga alloys prepared. In order to understand the chemical homogeneity in the homogenized button-like ingot, the specimens cut from the bottom center, the top center and the rim of the largest circumference of the alloy no. 35, Table 1, were tested by DSC and their Ms temperatures were found to be 355.2, 356.1 and 355.4 K, respectively [13]. This indicates that the chemical homogeneity is rather good in homogenized ingots. In this study, specimens cut from the bottom center of homogenized ingots were used for DSC and EPMA tests and the compositions given were the average of EPMA data for at least five readings.

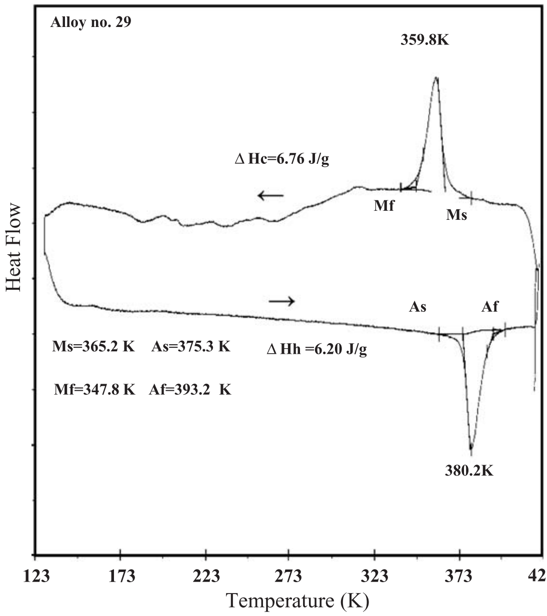

Fig. 1. DSC curve of Alloy no. 29. Temperatures of Ms, Mf, As and Af, and values of ΔHc and ΔHf are also shown.

The electron/atom (e/a) ratio of the alloys shown in Table 1 are higher than 7.47. Alloys having e/a ratio lower than 7.5 have their Ms temperature lower than 170 K and exhibit no significant transformation peak on the DSC curve.

In Table 1, the data of Ms, Mf, As, Af, Af–Ms (thermal hysteresis) and ΔH are all obtained from DSC curves. Data of alloy no. 29 are plotted in Fig. 1 for illustration. The data of Table 1 are used to examine the relationships of e/a vs. Ms temperature, e/a vs. ΔHc and Ms temperature vs. ΔHc. The linear regression technique with Microsoft Excel 2000 was utilized to analyze the quantitative relationship between Ms temperature (or ΔHc) and constituent elements in Ni–Mn–Ga SMAs.

3. Results and discussion

3.1. Effect of composition on Ms temperature and ΔHc

The Ni–Mn–Ga SMAs shown in Table 1 have Ni, Mn and Ga compositions in the range of 50.19–54.15, 19.52–29.79 and 19.84–26.24 at.%, respectively. The range of Mn in Table 1 is about 10 at.% (from 19.52 to 29.79 at.%), but those of Ni and Ga are only about 4–6 at.% in which the Ni content is higher than 50.1 at.% and the Ga content is lower than 26.3 at.%. This implies that off-stoichiometric Ni_2MnGa SMAs have the Ms temperature affected significantly by individual Ni and Ga contents and their effects are opposed. From the data of Table 1, the effects of composition on Ms temperature and ΔHc can be formulated by the linear regression listed as follows.

$$\mathrm{Ms(K)} = 25.44\mathrm{Ni(at.\%)} - 4.86\mathrm{Mn(at.\%)} - 38.83\mathrm{Ga(at.\%)} \quad (1)$$

$$\Delta\mathrm{Hc(J/g)} = 0.72\mathrm{Ni(at.\%)} - 0.16\mathrm{Mn(at.\%)} - 1.23\mathrm{Ga(at.\%)} \quad (2)$$

From the fact that the total contents of Ni, Mn and Ga in Ni–Mn–Ga SMAs are 100 at.%, Eq. (1) can be further formulated as follows.

$$\mathrm{Ms(K)} = 2544 - 30.30\mathrm{Mn(at.\%)} - 64.27\mathrm{Ga(at.\%)} \quad (3)$$

$$\mathrm{Ms(K)} = -486 + 30.30\mathrm{Ni(at.\%)} - 33.97\mathrm{Ga(at.\%)} \quad (4)$$

$$\mathrm{Ms(K)} = -3883 + 64.27\mathrm{Ni(at.\%)} + 33.97\mathrm{Mn(at.\%)} \quad (5)$$

The correlation coefficients, *R*-factors, of Eqs. (1) and (2) are 0.973 and 0.928, respectively. As seen in Eqs. (1)–(5), the effect of Mn on Ms and ΔHc is relatively small, as compared with those of Ni and Ga in Ni–Mn–Ga SMAs. At the same time, the effects of Ni and Ga are almost equal but opposite. Eq. (4) also indicates explicitly the reason why the Ni content is above ~ 50 at.%, but Ga content is below ~ 26 at.% in Ni–Mn–Ga SMAs having Ms >170 K. According to Eqs. (1) and (2), the stoichiometric Ni_2MnGa SMA has its Ms at 185 K (−88 °C) with ΔHc = 1.2 J/g. Also from Eq. (1), at a constant value of Mn content, the Ga addition will lower the Ms temperature; at constant Ni concentration, Mn addition will cause the Ms temperature to increase dramatically; and at constant Ga content, substitution of Ni by Mn will lower the Ms temperature significantly.

3.2. Relationship of Ms vs. e/a and ΔHc vs. e/a

From Table 1, the Ms and ΔHc values are plotted as a function of e/a in Figs. 2 and 3, respectively. Linear regression shows that the curve fitting is quite good in Figs. 2 and 3, with the *R*-factor as 0.987 for Fig. 2 and 0.977 for Fig. 3. The linear slopes of Figs. 2 and 3 are 891 K/(e/a) and 28 (J/g)/(e/a), respectively. This result is different from that reported in Ref. [14] in which the linear slope is 937 K/(e/a) with $R = 0.893$ for low Ms temperature alloys (Ms < 340 K and e/a: 7.35 ~ 7.66 with about 20 data points) and is 515 K/(e/a) with $R = 0.831$ for high Ms temperature alloys (Ms >360 K and e/a: 7.67 ~ 8.10 with seven data points). The discrepancy between this study and Ref. [14] remains unclear but may arise from the selective e/a (i.e. composition) range for linear regression analysis.

The *R*-factor of Fig. 3 is lower than that of Fig. 2, indicating that the data of ΔHc vs. e/a have more scatter than those of Ms vs. e/a. The reasons behind

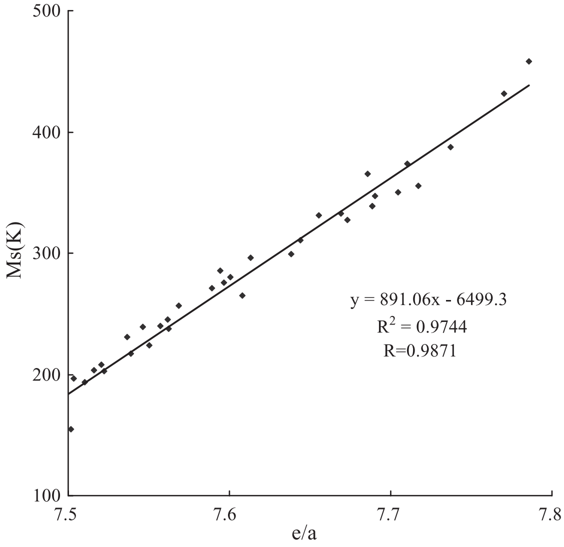

Fig. 2. Ms vs. e/a for the data in Table 1.

this scatter can be explained as follows. According to microstructural studies, Ni–Mn–Ga SMAs with various e/a values have different transformation sequences and can yield different martensite/premartensite, such as non-modulated BCT (body-centered tetragonal structure), 5-layered modulated martensite 10 M and 7-layered modulated martensite 14 M [15,16] Different transformation sequences may give different ΔHc values, but this kind of difference has not been considered in Fig. 3 and could cause some scatter. However, the *R*-factor of Fig. 3 still reaches 0.977. This suggests that the ΔHc value for different transformation sequences, such as Heusler $L2_1 \rightarrow$ non-modulated BCT or $L2_1 \rightarrow 10$ M martensite, may almost be the same.

Fig. 4 plots the relationship between Ms and ΔHc. Linear regression analysis yields the slope of 31 K/(J/g) with an *R*-factor equal to 0.977. The linear relationship shown in Fig. 4 implies that the Ni–Mn–Ga SMAs undergo thermoelastic martensitic transformation [17]. This behavior has also been reported in TiNi SMAs for B2 → B19' martensite [18] and B2 → R premartensite [19].

From Table 1, the thermal hysteresis, Af–Ms, of Ni–Mn–Ga SMAs, is in the range of 8–33 K and has no linear relationship with e/a value. The same result was also reported in Ref. [12] and no conclusion can be obtained at the present time.

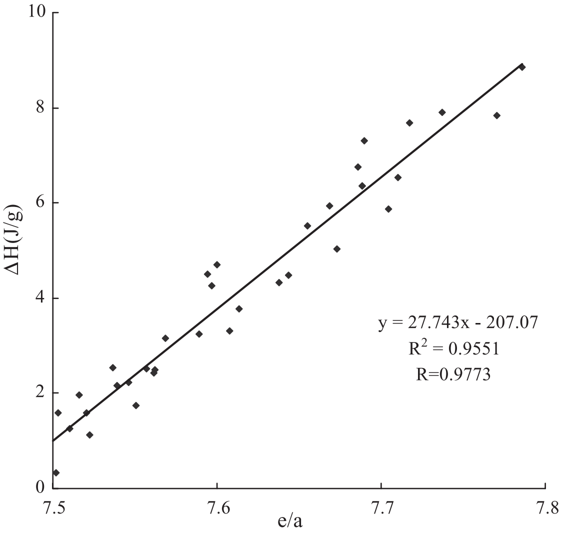

Fig. 3. ΔHc vs. e/a for the data in Table 1.

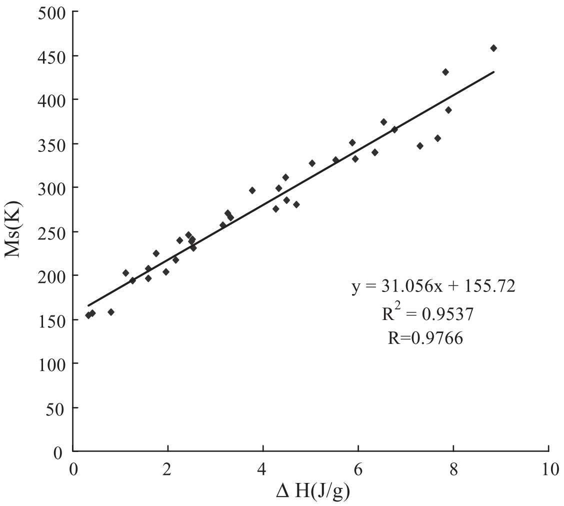

Fig. 4. Ms vs. ΔHc for the data in Table 1.

4. Conclusions

The Ni–Mn–Ga SMAs with Ms >126 K and amount of Ni, Mn and Ga being 50.19–54.15, 19.52–29.79 and 19.84–26.24 at.%, respectively, can be analyzed by linear regression and the following equations obtained.

$$\mathrm{Ms(K)} = 25.44\mathrm{Ni(at.\%)} - 4.86\mathrm{Mn(at.\%)} - 38.83\mathrm{Ga(at.\%)}$$

$$\Delta\mathrm{Hc(J/g)} = 0.72\mathrm{Ni(at.\%)} - 0.16\mathrm{Mn(at.\%)} - 1.23\mathrm{Ga(at.\%)}$$

These equations show that the effect of Mn content on Ms temperature is relatively small, but those of Ni and Ga are dramatic and their effects are opposite. The Ms and ΔHc of stoichiometric Ni_2MnGa SMA can be predicted as Ms = 185 K (− 88 °C) and ΔHc = 1.2 J/g, respectively. The linear relationship between Ms and ΔHc indicates that Ni–Mn–Ga SMAs undergo a thermoelastic martensitic transformation.

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