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Microstructure and phase transformations in a $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy with a high transformation temperature

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Abstract A Heusler $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy with a high transformation temperature has been obtained by substituting 5 at% Gd for Ga in a ternary $Ni_{50}Mn_{29}Ga_{21}$ ferromagnetic shape memory alloy. The microstructure and phase transformations in the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy have been investigated by scanning electron microscopy, transmission electron microscopy, X-ray diffraction and differential scanning calorimetry. It is shown that the microstructure of the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy consists of matrix and hexagonal Gd $(Ni,Mn)_4Ga$ phase, which indicates a eutectic structure composed of these two phases. One-step thermoelastic martensitic transformation occurs in this quaternary alloy. $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy exhibits a martensite transformation start temperature up to 524 K, approximately 200 K higher than that of $Ni_{50}Mn_{29}Ga_{21}$ alloy. At room temperature, non-modulated martensite with twin substructure is observed in $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy.

Introduction

During the past few years, ternary Ni–Mn–Ga ferromagnetic shape memory alloy (FSMA) has received more and more attention due to its large magnetic-field-induced strain (MFIS) and high response frequency, which makes it a potential candidate material for new magnetic actuators [1–4]. Unfortunately, the extreme brittleness of the Ni–Mn–Ga alloy precludes its use in practical applications. There has been growing interest in modifying Ni–Mn–Ga FSMA by adding rare earth elements to improve ductility. Tsuchiya et al. discovered that the addition of Nd significantly improved the compressive ductility of the alloy [5]. Zhao et al. reported that by adding rare earth Tb or Sm elements, the bending strength of NiMnGa alloys could be increased to some extent [6, 7]. However, the martensitic transformation temperature of Ni–Mn–Ga alloys containing Tb, Sm or Nb had small changes [5–7]. Recently, we reported that by adding Gd to a $Ni_{50}Mn_{29}Ga_{21}$ alloy, a significant improvement in the bending strength and ductility of the alloy was achieved [8]. At the same time, the substitution of Gd for Ga in a polycrystalline $Ni_{50}Mn_{29}Ga_{21}$ alloy notably increased the martensitic transformation temperature; the Ms of the alloy with 2 at% Gd was up to 390 K and still had a tendency to increase. The excellent ductility and higher martensitic transformation temperature make these alloys more attractive for practical applications. However, some problems still remain. For example, the crystal structure of the Gd-rich phase induced by adding Gd, and the effect of the increased Gd addition on the martensitic structure and transformation temperature are unknown. In the present paper, we increased the Gd concentration to 5 at% in order to determine the crystal structure of the Gd-rich phase and investigated the influence of the increased Gd content on the microstructure, crystal structure and phase transformation behavior of the $Ni_{50}Mn_{29}Ga_{21}$ alloy.

Experimental

The nominal compositions of the alloys studied were $Ni_{50}Mn_{29}Ga_{21}$ and $Ni_{50}Mn_{29}Ga_{16}Gd_5$. These alloys were

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prepared with high purity elements by melting four times in a non-consumed vacuum arc furnace under an argon atmosphere, and then cast into rods (10 mm in diameter and 75 mm in length) using a cylindrical copper mold set at the bottom of the furnace. The samples were annealed in vacuum quartz tubes at 1073 K for 24 h, and then water-quenched in order to get high ordering. The microstructures of the alloys were examined using a MX2600FE scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) analysis system. X-ray diffraction (XRD) measurements were performed using an X'Pert PRO MPD with CuKα radiation. The phase transformation temperatures were determined by Perkin-Elmer diamond differential scanning calorimetry (DSC); the rate of heating and cooling was 20 K/min. Thin-foil specimens for transmission electron microscopy (TEM) characterization were mechanically polished to about 80 μm and twin-jet electropolished with an electrolyte of nitric acid and methanol, 3:7 in volume, at around 258 K. An FEI TECNAI G^2 20 STWIN 200 kV transmission electron microscope equipped with a double-tilt cooling stage was used for TEM studies at room temperature.

Results and discussions

Figure 1 shows the backscattered electron images of the $Ni_{50}Mn_{29}Ga_{21}$ and $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloys. It is evident that the addition of Gd markedly changed the microstructure of the ternary $Ni_{50}Mn_{29}Ga_{21}$ alloy. The $Ni_{50}Mn_{29}Ga_{21}$ alloy exhibited a single-phase structure, whereas the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy contained a brightly imaging second phase. A eutectic structure composed of the matrix and the brightly imaging second phase was found in this alloy. A lamellar second phase was distributed within the grains and an irregular coarser second phase was observed along the grain boundaries. The compositions of both the matrix and brightly imaging second phase of the experimental alloys measured by EDS qualitative analysis are listed in Table 1. It can be seen that only ~1 at% Gd is detected in the matrix, which means the solid solubility of Gd in the matrix is very low. The Gd addition resulted in the formation of the Gd-rich phase along the grain boundaries or in the grains. As shown in Table 1, the Gd-rich phase consists of Ni, Mn, Ga and Gd. Compared with the composition of the matrix, the Mn content in Gd-rich phase is obviously decreased whereas the Gd content is increased. In order to determine the crystal structure of the Gd-rich phase, XRD measurements at 623 K were performed, as shown in Fig. 2. At this temperature, the $Ni_{50}Mn_{29}Ga_{21}$ alloy showed the parent phase with the $L2_1$ structure. However, in addition to the diffraction peaks of parent phase, some extra peaks were observed for the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy. Therefore, it was confirmed that these extra peaks belong to the Gd-rich phase. Since the XRD pattern of Gd-rich phase is rather similar to that of $GdNi_4Ga$ reported by Joshi [9], we attempted to index the diffraction peaks by reference to the $GdNi_4Ga$ phase. The lattice parameters of this phase are calculated to be $a = b = 0.5045$ nm, $c = 0.4085$ nm, slightly larger than that of $GdNi_4Ga$ phase. It is assumed that the existence of Mn atom in this phase may account for the increase of lattice parameters. Also, this phase has been further confirmed by TEM analysis. Figure 3a shows a TEM bright field image of the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy. It can be seen that the irregular Gd-rich phase (area A) is adjacent to the plate-like martensite. Its three SAED patterns, as shown in Fig. 3b–d, can be indexed as $CaCu_5$-type hexagonal structure with $a = b = 0.5045$ nm, $c = 0.4085$ nm and the space group of P6/mmm, which is consistent with the XRD

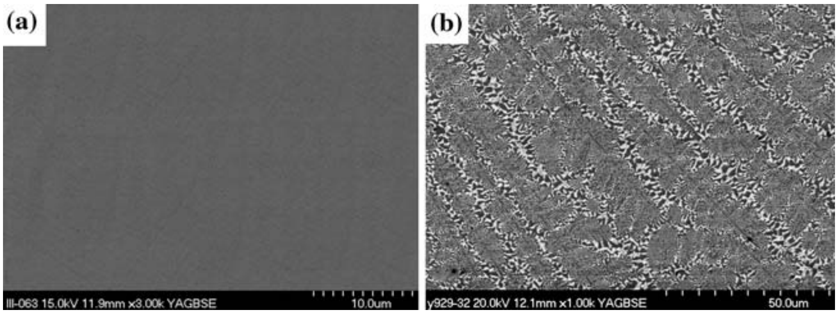

Fig. 1 Backscattered electron images of (**a**) the $Ni_{50}Mn_{29}Ga_{21}$ alloy and (**b**) the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy

Table 1 The EDS results of the $Ni_{50}Mn_{29}Ga_{21}$ and $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloys

Composition	Phase	Ni (at%)	Mn (at%)	Ga (at%)	Gd (at%)
$Ni_{50}Mn_{29}Ga_{21}$	Matrix	51	28	21	–
$Ni_{50}Mn_{29}Ga_{16}Gd_5$	Matrix	50	34	15	1
	Brightly imaging phase	53	14	18	15

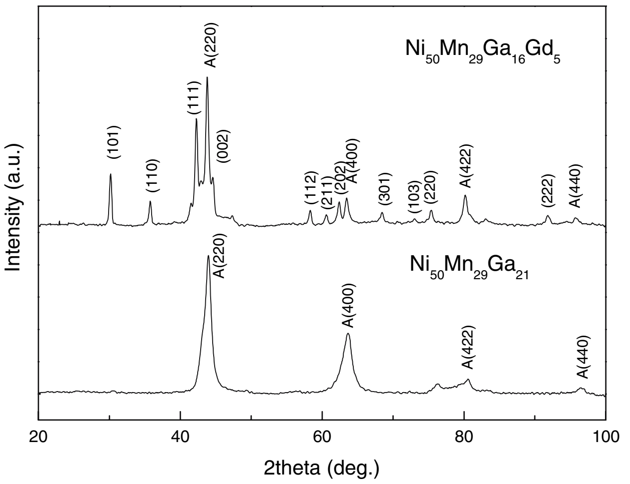

Fig. 2 XRD patterns of the $Ni_{50}Mn_{29}Ga_{21}$ and $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloys at 623 K

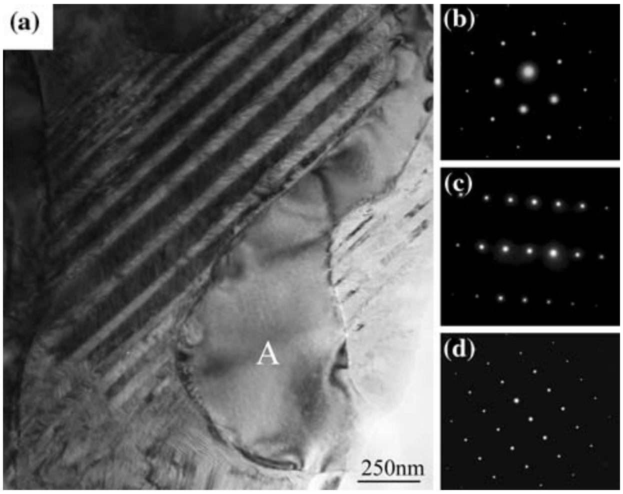

Fig. 3 TEM image of the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy and corresponding selected area electron diffraction patterns (**a**) bright field image (**b**), (**c**) and (**d**) SAED patterns taken from area A in (**a**)

results. The crystal type and space group of the Gd-rich phase in the studies alloy agree with those of $GdNi_4Ga$. Thus, the chemical formula of this phase may be approximately written as $Gd(Ni,Mn)_4Ga$. The existence of the $Gd(Ni,Mn)_4Ga$ phase in this $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy may have a strong effect on mechanical properties, which is the subject of an on-going investigation in our laboratory.

Figure 4 shows the DSC curves for the $Ni_{50}Mn_{29}Ga_{21}$ and $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloys. It can be seen that there is only one endothermic and exothermic peak during the heating and cooling processes for both alloys, indicating that one-step thermoelastic martensitic transformation still can be observed when up to 5 at% Gd is substituted for Ga. The transformation temperatures of the $Ni_{50}Mn_{29}Ga_{21}$ alloy are as follows: M_s = 326 K, M_f = 318 K, A_s = 323 K, A_f = 330 K, respectively. In the case of the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy, the transformation temperatures are M_s = 524 K, M_f = 501 K, A_s = 508 K, A_f = 539 K. It appears that the martensitic transformation temperatures increase notably with the Gd addition. The M_s of the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy is raised to 524 K, which is about 200 K higher than that of the ternary $Ni_{50}Mn_{29}Ga_{21}$ alloy. This value is the highest martensitic transformation temperature obtained in rare-earth-doped Ni–Mn–Ga alloys to date. The higher phase transformation temperatures indicate that this material may have great promise as high temperature shape memory alloy. The reason for the increase of the martensitic transformation temperatures in the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy may be explained as follows. The EDS results show that the composition in the matrix is changed due to the existence of the $Gd(Ni,Mn)_4Ga$ phase, as shown in Table 1. The content of Mn in the matrix is increased and the Ni content almost keeps constant, whereas the decrease of the Ga content occurs due to the substitution of Gd for Ga. This implies that the ratio of Mn and Ga increases when the content of Ni appears to be approximately unchanged, which can account for the increase of martensitic transformation temperatures. This is consistent with the results obtained by Albertini et al. [10] and Jiang et al. [11]. They found that the partial substitution of Ga by Mn at constant Ni concentration results in an increase of the martensitic transformation temperatures. In addition, the thermal hystereses of both alloys are calculated as a difference between reverse martensitic transformation finish temperature and martensitic transformation start temperature. For the $Ni_{50}Mn_{29}Ga_{21}$ and $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloys, the thermal hystereses are 4 and 15 K, respectively. It appears that thermal hysteresis is enlarged by the addition of Gd. Wang et al. reported that the thermal hysteresis in the NiMnGa alloys originates from the friction of phase boundary motion, and being only a small part of the latent heat of martensitic transformation [12]. Thus, it is speculated that the addition of 5 at% Gd to the ternary $Ni_{50}Mn_{29}Ga_{21}$ alloy increases the friction losses of phase boundary motion.

The X-ray diffraction patterns of the $Ni_{50}Mn_{29}Ga_{21}$ and $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloys at room temperature are presented in Fig. 5. For the $Ni_{50}Mn_{29}Ga_{21}$ alloy, the X-ray pattern exhibits five-layered martensite (5M) and the main reflections are indexed as a tetragonal structure with $a = b = 0.5936$ nm, $c = 0.5537$ nm ($c/a = 0.9328$). In contrast, typical non-modulated martensitic diffraction peaks are observed in the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy, indicating that the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy has a tetragonal martensitic structure without modulation (T martensite) at room temperature. The lattice parameters of martensite in this alloy are $a = b = 0.7626$ nm and $c = 0.6729$ nm. These values agree with the results reported in Ref. [13].

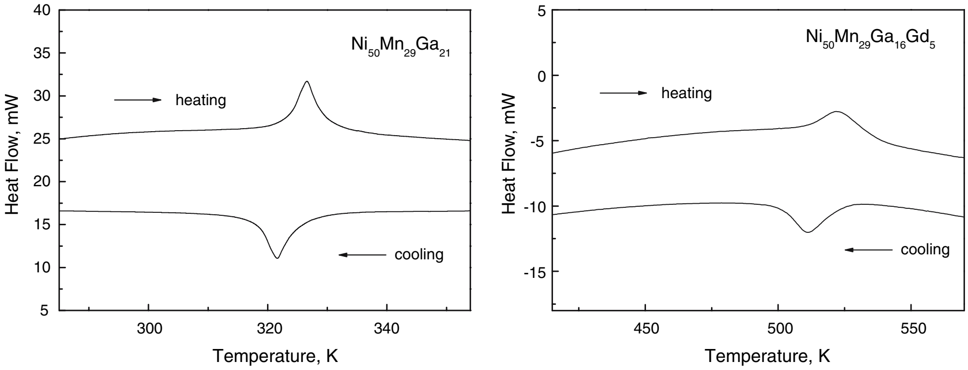

Fig. 4 DSC curves of the $Ni_{50}Mn_{29}Ga_{21}$ and $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloys

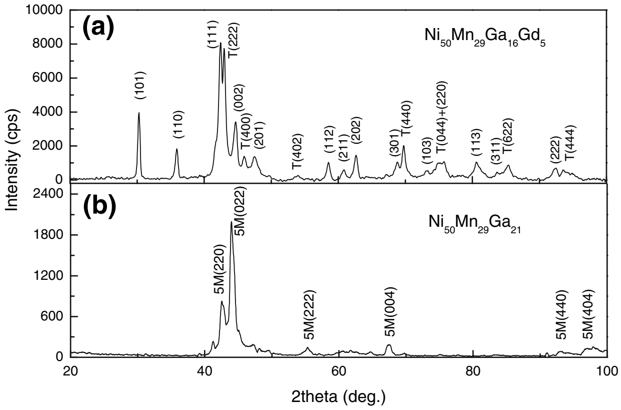

Fig. 5 X-ray diffraction patterns obtained at room temperature (**a**) $Ni_{50}Mn_{29}Ga_{16}Gd_5$ (**b**) $Ni_{50}Mn_{29}Ga_{21}$

A slight increase of the unit cell volume is observed by the Gd addition, which may be attributed to the substitution of the larger Gd atom for the smaller Ga atom. In the case of the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy, XRD data confirm the presence of T martensite and the Gd(Ni,Mn)$_4$Ga phase. This is in good agreement with the TEM results. Figure 6 shows a TEM bright field image and the SAED pattern of martensite in the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy. Figure 6a illustrates the typical microstructure, showing the stripe-like morphology of well-accommodated martensite plates. Every two variants show the typical twin relationship; the interface is distinct and straight. The SAED pattern exhibits {111} twins, as shown in Fig. 6b.

Conclusions

The effect of Gd addition on the microstructure and martensitic transformation behavior of a $Ni_{50}Mn_{29}Ga_{21}$ ferromagnetic shape memory alloy has been investigated. The results demonstrated that the microstructure of the $Ni_{50}Mn_{29}Ga_{21}$ alloy is notably altered by the addition of Gd. The microstructure of the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy consisted of the non-modulated tetragonal T martensite and the hexagonal Gd (Ni,Mn)$_4$Ga phase. A eutectic structure composed of these two phases was observed. One-step thermoelastic martensitic transformation occurs in this quaternary alloy. The addition of 5 at% Gd to the NiMnGa alloy increased the martensitic transformation temperature from 326 K to 524 K and broadened the thermal hysteresis from about 4 K to 15 K. Moreover, the addition of Gd also resulted in a change in the martensitic structure. At room

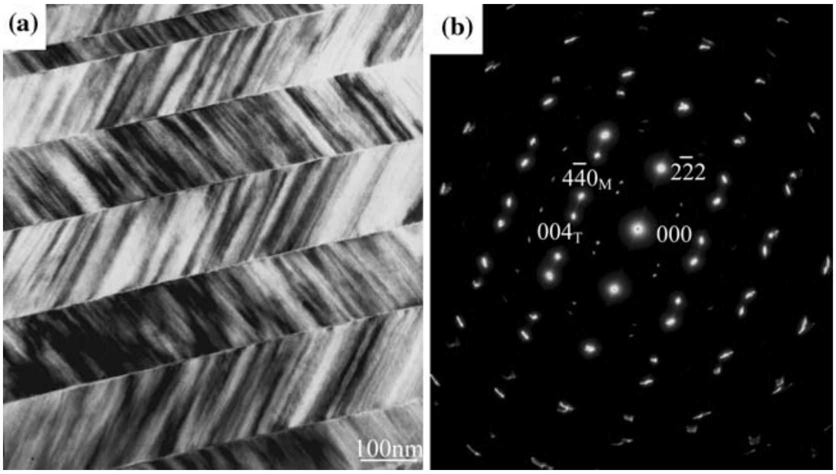

Fig. 6 Bright field image of martensite in the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy at room temperature (**a**) typical microstructure, (**b**) SAED pattern

temperature, five-layered martensite was observed in $Ni_{50}Mn_{29}Ga_{21}$ alloy whereas the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy exhibited a non-modulated martensite structure. Consequently, this observation concerning the $Ni_{50}Mn_{29}Ga_{16}Gd_5$ alloy may serve as a basis for the development of high temperature shape memory alloys from Ni–Mn–Ga alloys.

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