Mechanical and Magnetic Properties of Ni-Mn-Ga-Gd
Ferromagnetic Shape Memory Alloys
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The effects of rare earth Gd addition on the mechanical and magnetic properties of polycrystalline Ni50Mn29Ga21−xGdx (0 ≤ x ≤ 5) ferromagnetic shape memory alloys were investigated in detail. The results show that an appropriate amount of Gd addition significantly improves the mechanical properties of Ni-Mn-Ga alloy. When the Gd content is less than or equal to 1 at%, the compressive strength increases rapidly as Gd addition increases, and the subsequent increase slows down when the Gd content is in the range of 2 at%–5 at%. However, the compressive strain increases firstly and then decreases obviously. The Ni50Mn29Ga21 alloy exhibits the best overall mechanical performance among the Ni50Mn29Ga21−xGdx alloys (0 ≤ x ≤ 5) alloys. Moreover, Gd doping changes the fracture type of Ni-Mn-Ga alloy. The spontaneous magnetization of Ni50Mn29Ga21−xGdx alloys at 300 K and 4.2 K decreases with the increase of Gd content. The mechanism on the influence of Gd content on the mechanical and magnetic properties is discussed. [doi:10.2320/matertrans.M2015143]

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1. Introduction

During the past few years, Ni-Mn-Ga ferromagnetic shape memory alloys (FSMAs) have received more and more attention as potential microactuators because they show a large magnetic-field-induced strain (MFIS) up to 10% and a high response frequency (kHz).1–6 However, the relatively poor ductility and low strength of Ni–Mn–Ga alloys have triggered a great deal of interest. Improving mechanical property has become a priority in the development of Ni-Mn-Ga alloys. Recently, many attempts of alloying Ni-Mn-Ga alloys with rare earth elements have been carried out and some encouraging results have been achieved. The addition of rare earths can adjust the martensitic transformation temperatures. The decrease of martensitic transformation temperatures was observed in Ni-Mn-Ga-Sm alloy,7 while the martensitic transformation temperatures of Ni-Mn-Ga alloy containing Nd or Tb showed a small increase.8,9 The current group discovered that the martensitic transformation temperatures of Ni-Mn-Ga alloys increased remarkably by the substitution Dy or Y for Ga.10–12 Particularly, it was found that an appropriate addition of rare earth elements in polycrystalline Ni-Mn-Ga alloys, such as Dy, Y, Tb or Nd, can improve the compressive strength and ductility of the alloys.8,13,14 Furthermore, the bending strength of Ni-Mn-Ga alloy was increased with the addition of Tb or Sm to some extent.7,8,9

Heavy rare earth Gd is ferromagnetic and has the highest Curie temperature among the rare earth elements. Recently, the effect of the substitution of Gd for Ga on the martensitic and magnetic transitions in polycrystalline Ni50Mn29Ga21 alloy has been reported.15 Different martensitic phase transformations appear in different Gd content. Martensite structure changes from 5M with 0.1 at% Gd to 7M as the content of Gd continuously increases form 0.5 to 2 at%. The martensitic transformation temperatures increase markedly with increasing Gd content. Our research has demonstrated the martensitic transformation start temperature (Ms) of the alloy with 5 at% Gd was up to 524 K, approximately 200 K higher than that of Ni50Mn29Ga21 alloy.16 While the Curie temperature almost remains unchanged at low-Gd content and subsequently decreases obviously. It was also found that by adding 0.5 and 2 at% Gd to a Ni50Mn29Ga21 alloy, a significant enhance in the bending strength of the alloy was achieved, whereas the addition of 2 at% Gd leaded to the decrease of the bend strength compared with that of Ni50Mn29Ga20.5Gd0.5 alloy.17 However, little information on the effect of the larger range of Gd addition on the mechanical properties and fracture behavior is available up to now. In addition, in order to obtain large magnetic-field-induced-strain, large saturated magnetization is a key factor. But, the effect of adding Gd on the magnetization is unknown. Therefore, the present paper focuses on the influence of Gd addition in Ni50Mn29Ga21−xGdx (0 ≤ x ≤ 5) alloys on the microstructure, mechanical and magnetic properties.

2. Experimental

The nominal composition of the alloys was Ni50Mn29−
Ga21−xGdx (x = 0, 0.1, 0.5, 1, 2, 5). These alloys were prepared with high purity element by melting four times in a non-consumed vacuum arc furnace under 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 800°C for 24 h, followed by water-quenching. Microstructures of the alloys were examined using an Olympus metallographic microscope and an MX2600FE scanning electron microscopy (SEM) equipped with an X-ray energy dispersive spectroscopy (EDS) analysis system. The compression tests were performed at room temperature on an Instron 5569 testing system at a crosshead displacement speed of 0.05 mm min−1, and the size of the sample was

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3 mm × 3 mm × 5 mm. Fractography was observed by MX2600FE SEM to study the dominant fracture behavior in this alloy system. Saturation magnetization measurements were taken using the physical property measurement system (Quantum Design) in an applied field up to 3 T.

3. Results and Discussions

3.1 Microstructure of Ni50Mn29Ga21-xGd_x alloys

Figure 1 shows the optical micrographs of Ni50Mn29Ga21-xGd_x alloys (x = 0, 0.5, 2, 5). It is shown that the average grain size of ternary Ni50Mn29Ga21 alloy is approximately 110 µm. When the Gd content increases from 0.5 at% to 2 at%, the grain size is reduced from approximately 48 µm to 8 µm, as seen in Fig. 1(b) and (c). Apparently, the addition of Gd results in the grain size reduces significantly. Moreover, the grain size tends to be smaller with higher Gd content. Compared with the grain size of Ni50Mn29Ga21-Dy_x alloy with the same composition, the grain refinement effect of rare earth Gd is more obvious. Moreover, the second phase appears along the grain boundaries when the content of Gd is 0.5 at%. With increasing Gd content, the amount of the second phase increases gradually. A network-like distribution and local enrichment of the second phase are observed in Ni50Mn29Ga19Gd2 alloy. As the content of Gd increases to 5 at%, the matrix is divided into many islands owing to the further increase of the second phase. At the same time, a eutectic-like structure appears.

Our previous research demonstrates that the backscattered electron images of Ni50Mn29Ga21-xGd_x alloys (x = 0, 0.1, 0.5, 1, 2) alloys. The addition of Gd markedly changes the microstructure of the ternary Ni50Mn29Ga21 alloy. The Ni50Mn29-Ga31 alloy exhibits a single-phase structure, whereas the microstructure of the alloys containing Gd consists of the matrix and the white second phase. With increasing Gd content, the second phase firstly disperses homogeneously in the matrix with small amounts and then tends to segregate at the grain boundaries. When the content of Gd reaches 2 at%, the second phase interconnects gradually and form a network-like distribution, which consistent with the results of optical microscopy Fig. 1(c). Figure 2 shows the backscattered electron images of Ni50Mn29Ga16Gd5 alloy. A representative eutectic structure composed of the matrix and the second phase is observed in the alloy. As shown in Fig. 2(b), the second phases inside the grains have a lamellar morphology, and indicate radial growth; whereas those along the grain boundaries are of irregular shape with larger size. Figure 3 displays the line-scanning results of Gd, Ni, Mn and Ga elements in Ni50Mn29Ga19Gd2 alloy. Compared with the composition of the matrix, the second phase has a larger concentration of Gd and a smaller concentration of Mn, while the Ni and Ga content remain almost unchanged. The compositions of both the matrix and the white second phase of the experimental alloys measured by EDS qualitative analysis are listed in Table 1. It can be seen that the solid solubility of Gd in the matrix is very low, insolvable Gd element mostly forms the Gd-rich phase. As shown in Table 1, with the increasing of the Gd content, the composition of the Gd-rich phase keep unchanged mostly, while it has a certain influence on the composition of the matrix. Especially, the Mn content of the matrix is increased gradually with the increase of Gd content. According to the XRD and TEM measurements results, the Gd-rich precipitates can be indexed to Gd(Ni, Mn)_4Ga phase with a hexagonal CaCu5 type structure.
3.2 Mechanical properties of Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{21}\textsuperscript{x}Gd\textsubscript{x} alloys

Figure 4 shows the compressive stress-strain curves of Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{21}\textsuperscript{x}Gd\textsubscript{x} (x = 0, 0.1, 0.5, 1, 2, 5) alloys at room temperature. All the samples were in the martensite at room temperature, and were compressed to fracture. The effect of Gd content on the compressive strength and the compressive strain of Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{21}\textsuperscript{x}Gd\textsubscript{x} alloys are illustrated in Fig. 5. It is shown that the Gd content has a great effect on the compressive strength and strain of Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{21}\textsuperscript{x}Gd\textsubscript{x} alloys. When the Gd content is less than 1 at\textsuperscript{o}%, the compressive strength increases almost linearly as Gd addition increases, and the subsequent increase slows down when the Gd content is in the range of 2 at\textsuperscript{o}%-5 at\textsuperscript{o}%. The compressive strength of Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{21}Gd\textsubscript{1} alloy just raises slightly compared with that of Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{20}Gd\textsubscript{1} alloy. As the Gd content further increases to 5 at\textsuperscript{o}%, the growing extent enhances again. However, the compressive strain increases firstly and then decreases obviously. A maximum value of the compressive stain is obtained with 1 at\textsuperscript{o}% Gd addition. In general, the Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{20}Gd\textsubscript{1} alloy exhibits the best overall mechanical performance among the Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{21}\textsuperscript{x}Gd\textsubscript{x} alloys. A similar phenomenon has been reported in Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{21}Dy\textsubscript{1} alloys.\textsuperscript{13) For the two system alloys, the best comprehensive mechanical property is obtained in the alloy with the addition of 1 at\textsuperscript{o}% rare earth. A compressive strength of 1124.42 MPa with a compressive strain up to 16.25\% is achieved in Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{20}Gd\textsubscript{1} alloy. The compressive strength in the Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{20}Gd\textsubscript{1} alloy (1124.42 MPa) is approximately three times that of Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{21} alloy, and higher than that of Ni\textsubscript{49.18}Mn\textsubscript{28.14}Ga\textsubscript{21.58}Tb\textsubscript{1.1} alloy (500 MPa) by directional solidification.\textsuperscript{18) Furthermore, the compressive strength and strain of Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{20}Gd\textsubscript{1} alloy are all higher than those of Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{20}Dy\textsubscript{1.13)}

The reason for the improvement of mechanical properties in Ni\textsubscript{50}Mn\textsubscript{29}Ga\textsubscript{21}Gd\textsubscript{x} (x = 0~5) alloys is mainly due to the refinement of the grains, as shown in Fig. 1. Compared with rare earth Dy, the grain refinement of rare earth Gd is more apparent. Thus, the improvement of mechanical properties is better than that of adding Dy. The enhancement of the compressive strength may be closely related to the purifica-
tion of rare earth Gd. Rare earth easily reacts with the impurity elements, such as O and S, restraining the segregation of the impurities at the grain boundaries. The grain boundaries are consequently strengthened, which leads to an increase of the compressive strength. At the same time, the size and distribution of Gd(Ni, Mn)4Ga phase have a great effect on the compressive properties of Ni50Mn29-Ga21−xGdx alloys. The discontinuous distribution of the Gd(Ni, Mn)4Ga phase at the grains boundaries effectively hinders the movement of dislocations and the propagation of the cracks. More the volume fraction of Gd(Ni, Mn)4Ga phase is, more obvious the strength effect is. However, the network distribution and local enrichment of the Gd(Ni, Mn)4Ga phase is observed with the increase of Gd content, which results in the decrease of the compressive strain and gradual increase of compressive strength. For the Ni50Mn29-Ga21−xGdx alloy, the volume fraction of Gd(Ni, Mn)4Ga phase increases continually. Since the crack easily forms and propagates along the phase interface. Further increase of phase interface may be a reason for the sharp reduces of compressive strain. Moreover, a eutectic structure composed of the matrix and Gd(Ni, Mn)4Ga phase is found in the alloy. The two phases inside the grains indicates the lamellar distribution, and have small spacing. The existence of flaky brittle Gd(Ni, Mn)4Ga phases strongly restrains the deformation of martensite phase, which leads to the highest compressive strength and the lowest compressive strain.

Figure 6 shows the fractographs of Ni50Mn29Ga21−xGdx (x = 0.1, 1, 5) alloys at room temperature. As can be seen from the Fig. 6(a), the fractograph of doped 0.1 at% Gd alloy shows mixed morphology of intergranular fracture and cleavage fracture. As shown in A region of Fig. 6(a), it shows the typical brittle fracture along the columnar grain boundaries. In addition, some tearing edges appear in partial region, as shown in the area B of Fig. 6(a). This implies that certain plastic deformation occurs before fracturing. When the Gd content is increased to 1 at%, as shown in Fig. 6(b), the proportion of ductile tearing ridge increases significantly. This accounts for the Ni50Mn29Ga20Gd1 alloy possesses the higher strength and maximum compressive strain. Figure 6(c) and (d) show fractographs of Ni50Mn29Ga16Gd5 alloy. Figure 6(d) is the magnification of region A in Fig. 6(c). The fracture surface displays a dense and broken-crystal morphology. The microstructure of the alloy shows that the increased Gd(Ni, Mn)4Ga phase divides the matrix into many small regions. Under external stress, it is hard for brittle Gd(Ni, Mn)4Ga phase to deform plastically. Therefore, the stress concentration generates easily along the phase interface of the matrix and Gd(Ni, Mn)4Ga phase, which leads to the formation and propagation of cracks. As shown in Fig. 6(d), the brittle Gd(Ni, Mn)4Ga phase is stripped along the phase interface. So, for the Ni50Mn29Ga16Gd5 alloy with excessive Gd addition, interphase fracture leads to the increase of the brittleness.

Figure 7 shows the initial magnetization curves of Ni50Mn29Ga21−xGdx alloys at 300 K. According to the DSC results, the Ni50Mn29Ga21−xGdx alloys are all in the martensite phase at 300 K. As seen from the cures, the magnetization of Ni50Mn29Ga10Gd2 alloy increases slowly with the increase of magnetic field, and it is not still saturated even when the magnetic field is up to 3 T. However, the magnetization curves of Ni50Mn29Ga1xGdx (x = 0, 0.1, 0.5, 1) alloys exhibit typical characteristics of ferromagnetic materials. When the magnetic field is up to 1 T, the alloys reach the saturation magnetization. It is notable that the Gd-doping has a strong effect on the saturation magnetization of Ni50Mn29Ga21−xGdx alloys. The saturation magnetization of Ni50Mn29Ga21 alloy at 3 T magnetic field is 53.33 emu/g. When the content of Gd increases from 0.1 at% to 1 at%, the saturation magnetization approximately decreases linearly, which decreases from 48.12 emu/g to 36.09 emu/g. As the content of Gd is up to 2 at%, the spontaneous magnetization at 3 T magnetic field is just 15.7 emu/g. The initial magnetization curves of Ni50Mn29Ga1−xGdx alloys at 4.2 K are shown in Fig. 8. The magnetization of Ni50Mn29Ga21 alloy closes to the saturation when the magnetic field is 1 T. But, the saturated magnetic field is approximated 1.5 T when x = 0.1 and 0.5. The saturation magnetization at 3 T almost remains unchanged as the content of Gd is no more than 0.5 at%. For the Ni50Mn29Ga20Gd1 and Ni50Mn29Ga20Gd5 alloy, the magnetizations at 3 T are still not saturated and decrease obviously with the increase of Gd content. In addition, the magnetizations of Ni50Mn29Ga21−xGdx (x = 0, 0.1, 0.5, 1) alloys at 4.2 K under 3 T magnetic field are all higher than those at 300 K.

Based on our previous results of ac susceptibility measurement, a minor Gd addition, i.e. no more than 1 at%, has little influence on the Curie temperature. However, when the content of Gd is up to 2 at%, the Curie temperature decreases from 351 K for the undoped alloy to 326 K. The M-H curves of Ni50Mn29Ga21−xGdx (x = 0–2) alloys at 300 and 4.2 K exhibit that the alloys are ferromagnetic, which is consistent
with the results obtained by ac susceptibility measurement.\textsuperscript{15} Considering that the magnetization of the Ni$_2$MnGa Heusler alloy is mainly determined by the magnetic exchange interaction between Mn atoms,\textsuperscript{19} the reason for the decrease of the saturation magnetization by adding Gd can be explained as follows. On the one hand, based on the experimental results, the Gd addition causes the formation of Gd(Ni, Mn)$_4$Ga phases, which contains lower Mn compared with the nominal composition of Ni$_{50}$Mn$_{29-x}$Ga$_{21}$ alloys. The formation of Gd(Ni,Mn)$_4$Ga phases results in a significant Mn enrichment in the matrix. Furthermore, the volume fraction of this phase increases gradually with the increasing of Gd content. This leads to a continual increase of Mn content in the matrix. As shown in Table 1, the content of Mn in the matrix increases from 27.91 at\% for ternary Ni$_{50}$Mn$_{29}$Ga$_{21}$ alloy to 32.05 at\% for the 2 at\% Gd-doped alloy. In the same time, the decrease of the Ga content occurs due to the substitution of Gd for Ga. Xu et al. reported that the spontaneous magnetization of Ni$_{50}$Mn$_{50-x}$Ga$_x$ (14 $\leq$ x $\leq$ 23) alloys decreases almost linearly with the decrease of the Ga content.\textsuperscript{20} Our current data are well consistent with the reports. The extra Mn atoms couple antiferromagnetically with the neighboring Mn atoms, which leads to the decrease of saturated magnetization. On the other hand, in the Ni–Mn–Ga alloy, the magnetic coupling of Mn–Mn has been completed through itinerant electron of Ni and Ga. In the present alloys, the content of Ga is decreased by instead of Gd, which causes the decrease of the conduction electron-reduced of pairs of Mn atoms. This weakens the exchange effect of Mn–Mn atoms, resulting in the decrease in the saturation magnetization. In addition, with
the increase of Gd content in Ni_{50}Mn_{29}Ga_{21-x}Gd_x alloy, the volume fraction of Gd(Ni, Mn)_2Ga phase increases gradually. According to the reports in the literature, the Curie temperature of the GdNi_2Ga alloy is 20 K. So, it can be inferred that the Gd(Ni, Mn)_2Ga is a paramagnetic phase at 300 K and a ferromagnetic one at 4.2 K. However, our experimental result is different from it. The Ni_{50}Mn_{29}-Ga_{17}Gd_2 alloy with large amount of Gd(Ni, Mn)_2Ga phase is still not saturated under 3 T magnetic field at 4.2 K, and it has the lowest magnetization at 3 T among the Ni_{50}Mn_{29}-Ga_{21-x}Gd_x alloys (0 ≤ x ≤ 2). This imply that a paramagnetic to ferromagnetic transformation does not happen below 20 K, the Gd(Ni, Mn)_2Ga phase is still a paramagnetic phase at 4.2 K. The decrease of saturation magnetization may also be derived from the continuous increasing of paramagnetic Gd(Ni, Mn)_2Ga phase. Therefore, the decrease of saturation magnetization by adding Gd can be attributed to the comprehensive effects of the above three aspects. With the increase of Gd content, the decrease of magnetization is mainly due to the exist of large paramagnetic Gd(Ni, Mn)_2Ga phase, such as Ni_{50}Mn_{29}Ga_{20}Gd_2 alloy. For the Ni_{50}Mn_{29}-Ga_{20}Gd_2 alloy, under 3 T magnetic field, it reaches the saturation magnetization at 300 K and not at 4.2 K, which may be related to paramagnetic Gd(Ni, Mn)_2Ga phase. Our experimental data, however, are not sufficient to make an unambiguous conclusion about the mechanism responsible for the change of spontaneous magnetization by adding Gd, and further investigation is still needed.

4. Conclusions

The effects of Gd addition on the microstructure, mechanical and magnetic properties of Ni_{50}Mn_{29}Ga_{21-x}Gd_x (0 ≤ x ≤ 5) ferromagnetic shape memory alloy were investigated. The results of mechanical properties show that an appropriate amount of Gd addition significantly improves the mechanical properties of Ni-Mn-Ga alloy. It is shown that when the Gd content is less than 1 at%, the compressive strength almost increases linearly as Gd addition increases, and the subsequent increase slows down when the Gd content is in the range of 2 at%~5 at%. However, the compressive strain increases gradually and reaches the maximum value with 1 at% Gd addition. Further increase of Gd content makes the compressive strain of the alloys decrease obviously. Among the Ni_{50}Mn_{29}Ga_{21-x}Gd_x (0 ≤ x ≤ 5) alloys, the Ni_{50}Mn_{29}Ga_2Gd_1 alloy exhibits the best overall mechanical properties. Moreover, Gd doping changes the fracture type from intergranular fracture of Ni_{50}Mn_{29}Ga_2 alloy to transgranular cleavage fracture of Ni-Mn-Ga-Gd alloy. For the Ni_{50}Mn_{29}Ga_1Gd_3 alloy, the interphase fracture is found, which results in the higher brittle. In addition, the Gd-doping has a strong effect on the spontaneous magnetization of Ni_{50}Mn_{29}Ga_{21-x}Gd_x alloys at 300 K. When the content of Gd increases from 0.1 at% to 1 at%, the saturation magnetization decreases gradually. The further increase of Gd makes the magnetization reduce significantly. However, under 3 T magnetic field, the saturation magnetization at 4.2 K almost remains unchanged as the content of Gd is no more than 0.5 at% and then decreases obviously with the further increase of Gd content.

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