Martensitic transformation and shape memory effect in a ferromagnetic shape memory alloy: Mn$_2$NiGa

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Heusler alloy Mn$_2$NiGa has been developed by synthesizing a series of ferromagnetic shape memory alloys Mn$_{25+x}$Ni$_{50-x}$Ga$_{25}$ ($x=0$–25). Mn$_2$NiGa exhibits a martensitic transformation around room temperature with a large thermal hysteresis up to 50 K and a lattice distortion as large as 21.3% and has a quite high Curie temperature of 588 K. The martensite shows a high-saturated field up to 2 T. The excellent two-way shape memory behavior with a strain of 1.7% was observed in the single crystal Mn$_2$NiGa. The magnetic-field-controlled effect created a total strain up to 4.0% and changed the sign of the shape deformation effectively. © 2005 American Institute of Physics [DOI: 10.1063/1.2158507]

In the last ten years, many ferromagnetic shape memory alloys (FSMAs) have been developed, such as Ni$_2$MnGa, Ni$_2$FeGa, Ni$_2$MnAl, Co–Ni–Ga, Ni–Co–Al, and Ni–Mn–Sn (Sb, In). Among those FSMAs, Ni$_2$MnGa has been the most studied, and there have been many reports on its structure, magnetic properties, martensitic transformation, magnetically controlled shape memory effect, and magnetic-field-induced strain (MFIS). Due to the low transformation and Curie temperatures of the stoichiometric Ni$_2$MnGa, many off-stoichiometric materials were developed. The studies have mostly been focused on the off-stoichiometric materials with high content of Ni and low content of Mn or with high content of Mn and low content of Ga. However, the Ni–Mn–Ga system alloy with high content of Mn and low content of Ni, especially when the content of Mn is higher than 40% (at. %), has rarely been studied. In this work, a series of samples with composition of Mn$_{25+x}$Ni$_{50-x}$Ga$_{25}$ ($x=0$, 5, 10, 12.5, 15, 20, 25) have been synthesized. Their structure, magnetic properties, and martensitic transformations have been studied systematically, which leads to the discovery of a ferromagnetic Heusler alloy Mn$_2$NiGa. For the stoichiometric Mn$_2$NiGa alloy, single crystals were also grown successfully. An excellent two-way shape memory effect was observed in this material.

The as-cast samples were prepared by arc melting pure metals in an argon atmosphere. The samples were then encapsulated under argon in quartz glass and annealed at 1073 K for 72 h and subsequently quenched in an ice-water mixture. The single crystals of Mn$_2$NiGa were grown by the Czochralski method at a rate of 20 mm/h. The structure of the samples was determined using powder x-ray diffraction (XRD). The magnetic susceptibility measurements were carried out to determine the martensitic transformation temperature and the Curie temperature of the materials. Other magnetic properties, such as saturation magnetization, were measured using a superconducting quantum interference device magnetometer in fields up to 5 T. The single crystals were oriented by Laue diffraction in back-reflection geometry. The strain of the samples in the [001] direction (growth direction) was measured by the standard strain-gauge technique.

The temperature dependence of the ac susceptibility of Mn$_{25+x}$Ni$_{50-x}$Ga$_{25}$ ($x=0$, 5, 10, 12.5, 15, 20, 25) alloys is shown in Fig. 1(a). It is clearly seen that all the Mn$_{25+x}$Ni$_{50-x}$Ga$_{25}$ alloys exhibit the thermoelastic martensitic transformation, and the transition temperatures ($T_m$) and Curie temperatures ($T_c$) vary with the composition. The highest $T_c$ of 588 K and $T_m$ of 270 K were observed in the alloy Mn$_2$NiGa. The dependence of the thermal hysteresis upon Mn is evident in Fig. 1(a), i.e., the thermal hysteresis dramatically increases with increasing Mn in the system of Mn$_{25+x}$Ni$_{50-x}$Ga$_{25}$. The largest hysteresis is 50 K for Mn$_2$NiGa, 35 K higher than that of Ni$_2$MnGa alloy. That implies higher energy consumed during motion of phase boundaries. Compared with Ni$_2$MnGa alloy, Mn$_2$NiGa has a much higher $T_c$, a $T_m$ around the room temperature and a much larger thermal hysteresis.

Figure 1(b) shows the $T_m$ and the $T_c$ as a function of composition. The $T_m$ shows a parabola-like behavior with increasing Mn from Ni$_{50}$Mn$_{25}$Ga$_{25}$ to Mn$_{50}$Ni$_{25}$Ga$_{25}$. The lowest $T_m$ is about 30 K for Mn$_{57.5}$Ni$_{57.5}$Ga$_{25}$ alloy. Usually investigators treat the electron concentration ($e/a$) dependence of $T_m$ in FSMAs based on the Hume–Rothery mechanism. In our series samples, increased Mn content in the range of $x=0$–12.5, the $T_m$ decreases with the $e/a$ from 7.5 to 7.125, which is consistent with the results reported by Chernenko. However, the samples in the composition range of $x=12.5$–25, with $e/a$ range of 7.125–6.75 make a different $T_m$ variation, increasing monotonically with the decrease of $e/a$. It seems that the $e/a$ dependence could not simply explain the $T_m$ variation in our Mn–Ni–Ga system. The other factors for the stability of parent phase should be considered. Different from $T_m$, the $T_c$ increases monotonously with increasing Mn from 370 to 588 K as shown in Fig. 1(b), which indicates that ferromagnetic couplings are enhanced by in-
creasing Mn throughout the whole composition range.

Figure 2 shows the powder XRD patterns for the as-cast ingot of Mn$_2$NiGa at 200 and 300 K, respectively. For the powder XRD pattern at 300 K, all diffraction peaks can be indexed well to a cubic structure with calculated lattice parameters of $a = b = c = 5.9072$ Å and $\alpha = \beta = \gamma = 90^\circ$ as shown in Fig. 2(a), which indicates a Heusler alloy of Mn$_2$NiGa. During indexing the characteristic peaks of the XRD pattern collected at 200 K; it is found that the original 220 cubic peak splits into (220)$_{\text{tetra}}$ and (022)$_{\text{tetra}}$ and the (400)$_{\text{cubic}}$ and (422)$_{\text{cubic}}$ peaks also split, as shown in Fig. 2(b). From these results we conclude that the cubic parent phase transfers to a tetragonal martensite phase with the lattice parameters, $a = b = 5.5272$ Å, $c = 6.7044$ Å.

One should note that the lattice constants of the tetragonal martensite phase in Mn$_2$NiGa alloys have the following changes, $a = b$ shrinks and $c$ elongates, in comparison with its parent phase, which is different from what happens in the Ni$_2$MnGa alloys. In Ni$_2$MnGa, after the phase transformation, the lattice parameter $a = b$ elongates and $c$ contracts. The maximum strain by the lattice distortion $c/a$ can then be estimated to be 8.46% and 21.3% in Ni$_2$MnGa and Mn$_2$NiGa respectively, which suggests, potentially, a much larger strain existing in Mn$_2$NiGa alloy. Obviously, the larger lattice deformation during the martensitic transformation requires more energy to overcome the friction during the motion of the phase boundaries, which may explain why larger thermal hysteresis exists in Mn$_2$NiGa than in Ni$_2$MnGa.

Figure 3(a) shows the temperature-dependent saturation magnetization ($M_s$) of a Mn$_2$NiGa single crystal in the temperature from 5 to 350 K. It can be seen that $M_s$ decreases upon martensitic transformation. This magnetization behavior is not consistent with that in Ni$_2$MnGa where the magnetization of martensite is higher than that of the parent phase. A similar phenomenon occurred in Ni–Mn–Sn system.\(^1\)

To get a deeper understanding of the magnetic properties of the Mn$_2$NiGa alloy at the different phases, the initial magnetization curves were measured at 275 K for the parent phase and martensite, as shown in the inset to Fig. 3(a). Both

FIG. 1. Temperature dependence of low-field ac magnetic susceptibility ($\chi''$) and composition dependence of Curie temperature ($T_c$) and martensitic transformation temperature ($T_m$) for samples Mn$_{25+x}$Ni$_{50-x}$Ga$_{25-x}$ ($x = 0, 5, 10, 12.5, 15, 20, 25$). (b).

FIG. 2. XRD patterns of Mn$_2$NiGa sample at 300 K for its parent phase (a) and at 200 K for martensite (b).

FIG. 3. Magnetization of Mn$_2$NiGa as a function of temperature in a field of 5 T (a). Inset shows the magnetizations of Mn$_2$NiGa sample measured at 275 K for its martensite and parent phase, respectively. Magnetization as a function of magnetic field for samples Mn$_{25+x}$Ni$_{50-x}$Ga$_{25-x}$ ($x = 5, 10, 12.5, 15, 20, 25$) at 300 K (b).
curves show a typical behavior of a ferromagnet, however, they also indicate a very different saturation field (or different magnetic anisotropy) and different $M_s$. For the parent phase the saturation field is about 0.3 T and the saturation magnetization is about 30.3 emu/g, whereas the saturation field increases to about 2.0 T and $M_s$ decreases to 28.28 emu/g for the martensite. In comparison with 0.8 T, the Martensite contracts about 1.7% in this transformation, indicating a good two-way shape memory behavior in the Mn$_2$NiGa martensite. During heating, the shape deformation of the sample was measured at 300 K for all the samples in the different applied field. Generally, the change of strain depends on the martensitic transformation near room temperature and has a high $T_c$ (588 K). In addition, Mn$_2$NiGa distinguishes itself from the well-known Ni$_2$MnGa alloy by showing a much larger c/a ratio and much broader thermal hysteresis. The excellent two-way shape memory effect with strain of 1.7% and field-controllable shape memory effect up to 4.0% have been also observed in single crystalline Mn$_2$NiGa. All the results presented in this article suggest that the Mn$_2$NiGa alloy may be a promising candidate for many applications.

In summary, a ferromagnetic shape memory alloy of Mn$_2$NiGa was discovered, which shows a martensitic transformation near room temperature and has a high $T_c$ (588 K). In addition, Mn$_2$NiGa distinguishes itself from the well-known Ni$_2$MnGa alloy by showing a much larger c/a ratio and much broader thermal hysteresis. The excellent two-way shape memory effect with strain of 1.7% and field-controllable shape memory effect up to 4.0% have been also observed in single crystalline Mn$_2$NiGa. All the results presented in this article suggest that the Mn$_2$NiGa alloy may be a promising candidate for many applications.

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