Negative and positive magnetocaloric effect in Ni–Fe–Mn–Ga alloy

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Abstract

The phase transition process and magnetic entropy change \( \Delta S \) of \( \text{Ni}_{54.5}\text{Fe}_{20}\text{Mn}_{24.5}\text{Ga}_{24.5} \) alloy were studied. Substitution of Fe for Ni increases the Curie temperature and decreases the temperature of martensitic phase transition. The transition from ferromagnetic martensitic to ferrormagnetic austenitic state leads to an abrupt increase of magnetization below 0.5 T and an abrupt decrease of magnetization above 0.5 T. The sign of \( \Delta S \) changes from positive to negative with increasing the applied field from 0.5 to 2 T. The maximal value of the positive magnetic entropy change \( \Delta S \) is about 3.1 J/kg K for the applied field from 0 to 0.5 T. The increase of applied field from 1.5 T results in a negative \( \Delta S \). The peak of negative \( \Delta S \) is \( \sim 2.1 \text{ J/kg K} \) for a field change of 2 T.

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1. Introduction

In recent years, the materials with large magnetocaloric effect (MCE) have attracted considerable attention because magnetic refrigeration techniques based on the MCE have been demonstrated as a promising alternative to conventional vapor-cycle refrigeration [1]. Many materials undergoing a first-order magnetic transition have shown a giant MCE. The typical representatives of them are \( \text{MnFeP}_{1-x}\text{As}_x \) [2], \( \text{MnAs}_{1-x}\text{Sb}_x \) [3], \( \text{Gd}_x\text{Si}_x\text{Ge}_{1-x} \) [4], \( \text{La(Fe}_{x}\text{Si}_{1-x})_{13} \) [5] alloys and so on. The ferromagnetic Heusler Ni–Mn–Ga alloys undergo a structural transition from tetragonal martensite to cubic austenite on heating or the reverse process on cooling. This structural transition can cause a considerable magnetic entropy change in \( \text{NiMnGa} \) alloys [6]. Recent studies [7–9] show that upon the adjustment of the composition, the martensitic transition temperature \( T_M \) increases and Curie temperature \( T_C \) decreases until they overlap into one first-order magneto-structural phase transition. This first-order magnetostructural transition can bring about large magnetic entropy change. The largest entropy change of 20 J/kg K was obtained in \( \text{Ni}_{2.18}\text{Mn}_{0.82}\text{Ga} \) alloy with first-order magneto-structural phase transition when the magnetic field changes up to 1.8 T [10].

Furthermore, Ni–Mn–Ga–Fe alloys have attracted much attention too [11–15]. Studies show the partial substitution of Mn or Ni element by Fe element can have effects on both the structural transition temperature and Curie temperature. But there are few reports about the magnetic entropy changes of Ni–Mn–Ga–Fe alloys.

We have reported the magnetocaloric effect of \( \text{Ni}_{55.5}\text{Mn}_{20}\text{Ga}_{24.5} \) alloy [16] previously. The Curie temperature \( T_C \) of the alloy is adjusted to the vicinity of martensitic transition temperature \( T_M \). The structural transition and magnetic transition occur simultaneously in the alloy. The entropy change of \( \text{Ni}_{55.5}\text{Mn}_{20}\text{Ga}_{24.5} \) alloy is as large as 15.3 J/kg K in the applied field of 2 T.

In this work, Ni element is partially replaced by Fe element in \( \text{Ni}_{55.5}\text{Mn}_{20}\text{Ga}_{24.5} \) alloy. We are interested in the effect of the substitution of Fe element on the transition...
temperatures, magnetic properties and magnetic entropy change.

2. Experimental procedure

Polycrystalline alloys were prepared from purity (99.9%) elements by arc melting in argon gas atmosphere. Each arc-melted ingot was flipped over and remelted three times. To obtain a single phase, the ingots were homogenized at 1173 K for 3 days, and then quenched in ice water.

The phase structure was confirmed at room temperature by X-ray diffraction with CuKα radiation. The sample for the magnetic measurement was cut from the middle part of the ingots. The martensitic transition temperature $T_M$ on cooling, the austenitic transition temperature $T_A$ on heating and Curie temperature $T_C$ were determined by alternating current susceptibility. The magnetization measurements were performed on a vibrating sample magnetometer (LakeShore-7410) with a maximum field of 2 T. The isothermal magnetic entropy change is calculated by Maxwell relation:

$$\Delta S_M = \int_{H_1}^{H_2} \left( \frac{\partial M(H, T)}{\partial T} \right)_H dH,$$

where $T$ is the temperature and $M$ is the magnetization.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the alloy. The result shows that the alloy crystallizes in the non-modulated tetragonal structure of martensite phase with a small amount of the austenitic phase.

Fig. 2 shows the temperature dependencies of the AC-susceptibility measured on the heating and cooling processes for Ni$_{55.5}$Mn$_{20}$Ga$_{24.5}$ and Ni$_{54.5}$FeMn$_{20}$Ga$_{24.5}$ alloys. The martensitic transition temperature $T_M$, the reverse transition temperature $T_A$ and Curie temperature $T_C$ of Ni$_{54.5}$FeMn$_{20}$Ga$_{24.5}$ are 311, 320 and 321 K, respectively; while for Ni$_{55.5}$Mn$_{20}$Ga$_{24.5}$, the corresponding parameters are 286, 292 and 341 K, respectively.

From Fig. 2, it can be found that the austenitic transition temperature $T_A$ is near the room temperature in the Ni$_{54.5}$FeMn$_{20}$Ga$_{24.5}$ alloy. It causes a little fraction of austenitic phase at the room temperature, as seen in Fig. 1.

From the AC-susceptibility results for Ni$_{55.5}$Mn$_{20}$Ga$_{24.5}$ alloy, it can be seen that some ferromagnetic martensite has transited to ferromagnetic austenite before the magnetic transition on the heating process. Then the mixed ferromagnetic martensite and austenite transited to paramagnetic austenite at the magnetic transition temperature. But on the cooling process, the paramagnetic austenite transited to ferromagnetic austenite first. Then ferromagnetic austenite transited to ferromagnetic martensite. But the replacement of Ni by Fe in Ni$_{54.5}$FeMn$_{20}$Ga$_{24.5}$ alloy...
element decreases the martensitic transition temperature from 311 to 286 K and increases Curie temperature from 321 to 341 K. It has been reported that $T_M$ increases with the electron concentration $e/a$ increasing [17,18]. The replacement of Ni by Fe results in a decrease of $e/a$ in the Ni$_{55.5}$Mn$_{20}$Ga$_{24.5}$ alloy because there are more d electrons in Ni element than that in Fe element. The decreasing of $e/a$ causes a decrease in the martensitic transition temperature. The results are in agreement with previous reports [17,18]. Furthermore, the increase of $T_C$ in Fe-containing sample implies that there are small magnetic moments located on Ni atoms in Ni–Mn–Ga alloy. The increase in $T_C$ in the alloy can be accounted for a stronger Fe–Mn exchange interaction as compared to the Ni–Mn one [19].

Fig. 3 shows the magnetization isotherms at the temperature near the phase transition for Ni$_{55.5}$Mn$_{20}$Ga$_{24.5}$ and Ni$_{54.5}$FeMn$_{20}$Ga$_{24.5}$ alloys. The curves indicate that these two alloys undergo different transition processes. The magnetization of Ni$_{55.5}$Mn$_{20}$Ga$_{24.5}$ alloy decreases with increasing temperature, especially near the temperature of phase transition, the magnetization decreases more rapidly. This phenomenon is attributed to the occurrence of the magnetic and structural transition from ferromagnetic martensite to paramagnetic austenite. But for Ni$_{54.5}$FeMn$_{20}$Ga$_{24.5}$ alloy, it is observed that the magnetization is hard to saturate below the structural transition temperature because magnetic anisotropy of the martensitic state is larger. While above the martensitic transition temperature, the magnetization is easy to saturate because magnetic anisotropy of the austenitic state is smaller than that of the martensitic state. The transition from the ferromagnetic martensitic to ferromagnetic austenitic state leads to an abrupt increase of the magnetization below 0.5 T and an abrupt decrease of magnetization above 0.5 T. Then there exist crossing points in the $M$–$H$ curves at the magnetic field about 0.5 T.

The magnetic entropy changes $\Delta S$ under different applied field from 0.5 to 2 T are calculated by Maxwell relation. The results are shown in Fig. 4. It is observed that the magnetic entropy change $\Delta S$ is positive for a field change below 1.5 T and negative for a field change above 1.5 T. The peak value of $\Delta S$ decreases with increasing applied field. The magnetic entropy change $\Delta S$ shows a maximal value about 3.1 J/kg K for the applied field is up to 0.5 T. Then the positive $\Delta S$ value is counteracted by the negative $\Delta S$ value with the field increasing. $\Delta S$ shows the negative value when the applied field increases to a sufficient value. The peak of negative $\Delta S$ about $-2.1$ J/kg K is obtained when the field is up to 2 T.

4. Conclusion

Substitution of Fe for Ni in Ni$_{55.5}$Mn$_{20}$Ga$_{24.5}$ alloy decreases the valence electron concentration, $e/a$, hence decreases the martensitic transition temperature $T_M$ and increases Curie temperature $T_C$. The fact that $T_M$ moves away from $T_C$ makes the concurrence of structural and
magnetic transition in Ni$_{55.5}$Mn$_{20}$Ga$_{24.5}$ alloy separate again. The transition from the martensitic to austenitic state leads to a discontinuous increase of magnetization below 0.5 T and a discontinuous decrease of magnetization above 0.5 T. So the magnetic entropy change $\Delta S$ exhibits a change from positive to negative. The positive $\Delta S$ is observed when the applied field is below 1.5 T. The maximum of the positive $\Delta S$ is about 3.1 J/kg K under the field of 0.5 T. The negative $\Delta S$ is observed when the applied field exceeds 1.5 T and the peak of the negative $\Delta S$ is about 2.1 J/kg K under the field of 2 T.

Acknowledgments

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References