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Magnetocaloric and negative thermal expansion effects for $Ni_{55.5}Mn_{19.5}Ga_{25}$ Heusler alloy with magneto-structural transition

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HIGHLIGHTS

- The $Ni_{55.5}Mn_{19.5}Ga_{25}$ exhibits martensitic transition with PM/FM type.
- A considerable refrigerant capacity was obtained around room temperature.
- The NTE of martensite performs an excellently linear and reversible feature.

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ABSTRACT

In the present work, the crystal structure, transforming property, magnetocaloric and negative thermal expansion effects were investigated in polycrystalline $Ni_{55.5}Mn_{19.5}Ga_{25}$ alloy, respectively. The structure measurement indicates that it possesses unmodulated martensitic structure ($L1_0$) at room temperature. Here, the present alloy shows a first-order magneto-structural transformation from paramagnetic (PM) austenite to ferromagnetic (FM) martensite on cooling. Benefiting from this transformation, a considerable refrigerant capacity (RC) with a value of about 55 J/kg K was obtained around room temperature for the magnetic field change of 3 T. Moreover, the unique negative thermal expansion (NTE) effect was observed not only for the transforming range, but also for the pure martensitic state of the studied alloy. As distinct from a large NTE effect caused by magneto-structural transformation, such an effect at martensite is not accompanied by any thermal hysteresis, performing an excellently linear feature with a coefficient over 8×10^{-6}/K within a broad temperature range (from 250 K to 50 K).

1. Introduction

In the recent years, Ni-Mn based ferromagnetic shape memory alloys (FSMAs) have become a subject for intensive investigations on experimentally and theoretically. Among these FSMAs, the stoichiometric Ni_2MnGa with ferromagnetic (FM) Heusler structure was the firstly discoverable and the mostly representative. During the cooling process, it first undergoes a pure magnetic transformation at Curie temperature (T_C) in the vicinity of 376 K at austenitic phase, and then experiences a first-order martensitic transformation (MT) at 202 K from the FM parent phase with $L2_1$ structure to the tetragonal martensitic phase maintaining its FM ordering with higher magnetocrystalline anisotropy [1]. Because of difference in anisotropy energy between the two phases, the Ni-Mn-Ga alloys usually exhibit multiple functional properties upon MT, such as giant field-induced shape memory effect (SME) [2,3], large magnetocaloric effect (MCE) [4,5], and magnetoresistance (MR) [6,7].

As is well known, both the T_C and T_M (martensitic transition temperature) for Ni-Mn-Ga alloys are very sensitive to their compositions. From the previous works [8,9], by the substitution of suitable Ni for Mn and suitable Mn for Ga in the stoichiometric Ni_2MnGa alloy, the MT shifts towards higher temperature range, while the pure magnetic transition moves to the lower temperature range. In some Ni-Mn-Ga with particular compositions, these two transitions can linked to be each other, forming a first order magneto-structural transformation occurred between paramagnetic (PM) austenitic and FM martensitic phases through the variation of temperature. In this case, a significantly large change of magnetization across MT can be obtained, which is similar to that

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observed in some giant magnetocaloric materials [10–14]. Thus, much attention has mainly focused on the improvement of their MCE to make these alloys more appropriate to magnetic refrigeration applications [5,15–21]. In addition to large MCE, for these particular alloys, a few studies were also found that a large spontaneous phase transition strain usually reveals a negative thermal expansion (NTE) effect [16,21,22]. Such a unique behavior is analogous to that reported for La(Fe,Co,Si)$_{13}$ and Mn-Co-Ge based compounds induced by a first order magneto-structural transformation [23,24]. Up to date, however, the Ni-Mn-Ga alloys have not been considered as NTE materials for practical applications due to the limited NTE coefficient, narrow temperature window as well as obvious thermal hysteresis upon MT. Based on these motivations, in the present work, we sought the optimized composition and synthesized polycrystalline $Ni_{55.5}Mn_{19.5}Ga_{25}$ Heusler alloy. The crystal structure, transforming property, magnetocaloric and negative thermal expansion effects were carefully investigated in this alloy. The mechanism behind these effects was also discussed in detail.

2. Experimental

2.1. Material synthesis

Polycrystalline $Ni_{55.5}Mn_{19.5}Ga_{25}$ alloy with nominal composition was prepared by repeated arc melting under argon atmosphere using Ni (4N, Alfa Aesar), Mn(3N, Alfa Aesar) and Ga (5N, Alfa Aesar) simple metals. The weight loss of obtained ingots after melting was found to be less than 1%. For homogenization, the prepared ingot was sealed in the evacuated silica tubes, heated at 1073 K for 3 days, and then slowly cooled to room temperature.

2.2. Material characterization

The crystal structure of this alloy at room temperature was carried out by powder X-ray diffraction using Rigaku Ultima-IV X-ray diffractometer. The magnetization data were collected from vibrating sample magnetometer (Versalab, Quantum Design). The thermal data were recorded by differential scanning calorimetry (DSC, Q2000, TA) measurement performed with a heating/cooling rate of 10 K/min. The thermal expansion property was examined by standard strain-gauge technique, using a rectangular specimen with a dimension of $2 \times 10 \times 10$ mm^3. In order to reduce the errors produced by metrical strain-gauge itself, we used another unloaded strain-gauge as a reference substance for the measurement.

3. Results and discussion

3.1. Crystal structure at room temperature

The X-ray diffraction pattern of $Ni_{55.5}Mn_{19.5}Ga_{25}$ measured at room temperature is shown in Fig. 1. The XRD pattern can be indexed with body-centered tetragonal structure, indicating a non-modulation martensite ($L1_0$) at room temperature for the studied alloy. Meanwhile, the reflections manifest that it possesses the lattice parameters with a = b = 7.673 Å, c = 6.674 Å and $\alpha = 90°$. According to these results, the calculated volume of unite cell at martensitic state is about 196.5 Å^3. Such a value is in fairly good agreement with the early experimental results [20,21] and slightly lower than that observed in the austenitic phase with $L2_1$ cubic structure for other Ni-Mn-Ga based alloys [1,18,25].

3.2. The property of martensitic transformation

Fig. 2(a) shows the temperature dependence of Magnetization

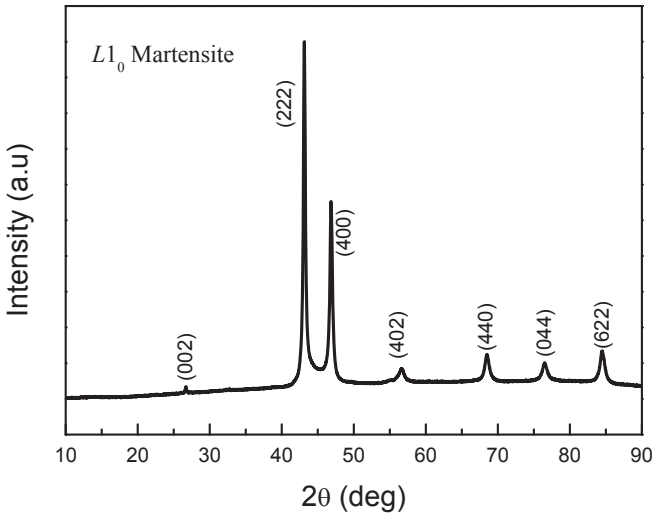

Fig. 1. The X-ray diffraction pattern of $Ni_{55.5}Mn_{19.5}Ga_{25}$ alloy measured at room temperature.

(M-T) for $Ni_{55.5}Mn_{19.5}Ga_{25}$ alloy on field-cooled cooling (FCC) and field-cooled warming (FCW) modes at a magnetic field of 5 mT. For the studied alloy, an abrupt jump of magnetization appears in the vicinity of the direct MT starting temperature (M_s), and then attains to a steady stage around the direct MT finishing temperature (M_f) on the FCC branch. On the FCW branch, a sudden drop of magnetization happens in the vicinity of the reverse MT starting temperature (A_s) and returns to its initial state around the reverse MT finishing temperature (A_f). These characteristic temperatures determined by exothermic and endothermic peaks from DSC measurement equal to $M_s = 316$ K, $M_f = 304$ K, $A_s = 312$ K, and $A_f = 327$ K, as described in Fig. 2(b). Between the FCC and FCW procedure, there exists a large thermal hysteresis, which suggests that the studied alloy undergoes a MT with first-order magneto-structural feature. Furthermore, the entropy as a function of temperature was computed by exothermic curve in terms of the following equation

$$S(T) = \int_{T_1}^{T_2} \frac{1}{T}\left(\frac{dQ}{dT}\right) dT \quad (1)$$

where both the T_1 and the T_2 denote the temperature well below and above the phase transition, respectively, and dQ/dT is the heat capacity. The Eq. (1) can be calculated with numerical method, and the final results are described in Fig. 2(c). From this figure, one can notice that the transition entropy change (ΔS_{tr}) obtained during direct MT amounts to about 28 J/kg K, which is comparable to those of giant magnetocaloric compounds [10–13]. It is predicted that the studied alloy may be a promising candidate for magnetic refrigeration.

3.3. Magnetocaloric effect

In order to confirm this point as mentioned above, the isothermal magnetic entropy changes ΔS_M during direct MT under different magnetic fields for $Ni_{55.5}Mn_{19.5}Ga_{25}$ alloy are illustrated in Fig. 3. In order to avoid the mixed phases disturbing the final results, the ΔS_M was calculated from the M-T curves (see the inset of Fig. 3) at various magnetic fields by using the Maxwell relation,

$$(\partial M/\partial T)_H = (\partial S/\partial H)_T \quad (2)$$