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Phase formation characteristics and magnetic properties of bulk Ni_2MnGe Heusler alloy

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ABSTRACT

We have systemically studied the effects of annealing temperature and alloy composition on the structural and magnetic properties of bulk Ni_2MnGe and $Ni_{2.1}Mn_{0.9}Ge$ Heusler alloys. We have observed that both annealing temperature and the alloy composition drastically alter the phases found in the samples due to the presence of competing ternary phases. Annealing at 900 and 950 °C for both alloy compositions facilitate the formation of $L2_1$ Heusler phase. Nevertheless, formation of $Ni_5Mn_4Ge_3$ and $Ni_{16}Mn_6Ge_7$ phases cannot be prevented for Ni_2MnGe and $Ni_{2.1}Mn_{0.9}Ge$ alloys, respectively. In order to estimate the magnetic contribution of the $Ni_5Mn_4Ge_3$ impurity phase to that of the parent Ni_2MnGe, we have also synthesized pure $Ni_5Mn_4Ge_3$ alloy. Antiferromagnetic nature of $Ni_5Mn_4Ge_3$ with low magnetization response allows us to reveal the magnetic response of the stoichiometric bulk Ni_2MnGe. Bulk Ni_2MnGe shows simple ferromagnetic behavior with a Curie temperature of 300 K, in agreement with the previous results on thin films. Despite the divergence of magnetization curves between field cooled (FC) and field heated (FH) modes, stoichiometric Ni_2MnGe alloy does not undergo a martensitic phase transition based on our variable temperature X-ray diffraction experiments.

1. Introduction

Ni–Mn based Heusler alloys constitute a prime family of compounds that have been studied extensively due to the presence of a magnetostructural phase transition which makes them useful for magnetic refrigeration and magnetic shape memory applications such as actuators [1–3]. Upon cooling, Ni–Mn–Z (where Z = Ga, In, Sn, Sb) undergo a phase transition into a martensitic phase. Only for Ni_2MnGa phase, martensitic phase transition occurs for the stoichiometric Heusler composition in the ferromagnetic state. Associated with the first order martensitic phase transition, (magnetic) shape memory effects are observed in these alloys. Magnetic and structural phase transition temperatures can be tailored to yield large caloric effects, which makes them useful for magnetic refrigeration applications [1].

Despite the abundance of studies on other Heusler compositions, there have been relatively few studies on Ni_2MnGe both in bulk and thin film form. Lund et al. have reported the growth of thin films of Ni_2MnGe using Molecular Beam Epitaxy (MBE) and obtained ferromagnetic films with a Curie temperature of 300 K [4]. Kim et al. have grown Ni_2MnGe films using flash evaporation. Their films were ferromagnetic with a Curie temperature of 280 K [5]. Only Oksenenko et al. have reported the structural and magnetic properties of stoichiometric bulk Heusler composition Ni_2MnGe [6]. They could not obtain a pure Heusler phase and observed complex magnetization behavior accordingly. Si et al. synthesized bulk $Ni_{2.1}Mn_{0.9}Ge$ and $Ni_{22}Mn_{0.8}Ge$ [7]. They claimed to obtain pure off-stoichiometric Heusler phase. Their magnetic measurements show a simple ferromagnetic behavior with an ordering temperature T_C of 246 K for $Ni_{2.1}Mn_{0.9}Ge$ and 151 K for $Ni_{22}Mn_{0.8}Ge$.

The key property that renders other Ni–Mn based Heusler alloys useful for applications is the presence of a first-order martensitic phase transition from high temperature $L2_1$ phase to a low temperature martensite phase [1]. Zayak et al. predicted an instability of $L2_1$ structure in Ni_2MnGe alloys using first-principles calculations but this has not been observed so far [8]. Recently, there has been another prediction [9], suggesting the likelihood of a transition from the cubic austenite phase to a tetragonal martensite phase. We have undertaken a systematic study to clarify the structural and magnetic properties of stoichiometric bulk Ni_2MnGe and to address the martensitic phase transition predictions. In addition to the stoichiometric composition, we have also synthesized $Ni_{2.1}Mn_{0.9}Ge$ alloy, in order to reproduce the pure $L2_1$ Heusler

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phase claimed in ref. [7]. Another off-stoichiometric sample with the determined composition of $Ni_{1.91}Mn_{0.94}Ge_{1.15}$ was also used to study the effect of Ni off-stoichiometry and demonstrate the effect of annealing temperature. We have observed that annealing temperature and alloy composition significantly affect the phases encountered in the alloys. Finally, we show the lack of a martensitic phase transition using variable temperature X-ray diffraction experiments.

2. Experimental

Ni_2MnGe, $Ni_{2.1}Mn_{0.9}Ge$, $Ni_5Mn_4Ge_3$ and $Ni_{1.91}Mn_{0.94}Ge_{1.15}$ alloys were synthesized by arc-melting the constituting elements under Ar atmosphere using an Arc Melter. The alloys were melted 5 times to assure melt homogeneity. Ni_2MnGe and $Ni_{2.1}Mn_{0.9}Ge$ alloys were annealed first at 900 °C for 3 days in order to reproduce the synthesis conditions in ref. [7] and then subsequently annealed at 950 °C for 4 days to see the effects of higher temperature on the stability of phases. $Ni_5Mn_4Ge_3$ alloy was annealed at 800 °C for 6 days following Ref. [10]. $Ni_{1.91}Mn_{0.94}Ge_{1.15}$ was annealed at 800 °C for a week and then subsequently annealed at 950 °C for another week. Annealing was done with samples closed in quartz tubes under Ar atmosphere and alloys were quenched in ice water. Composition of the alloys were checked using Energy Dispersive X-ray Spectroscopy(EDS) with a Zeiss EVO 40 Scanning Electron Microscope (SEM). Crystal structure of the alloys were determined using X-ray diffraction experiments with a Rigaku D-Max 2200 diffractometer with Mo K-alpha radiation at room temperature. Variable temperature X-ray diffraction experiments were carried out using a Rigaku Smartlab diffractometer having a Cu K-alpha source equipped with a commercial temperature attachment, between 83 and 573 K. Le Bail fits to the X-ray diffraction data were done using GSAS software package [11]. Magnetization of the samples were measured in a MPMS magnetometer between 10 and 380 K.

3. Results and discussion

Fig. 1 shows the Le Bail fit of the X-ray diffraction data of the stoichiometric Ni_2MnGe alloy annealed at 900 °C for 3 days collected at room temperature. All peaks can be indexed with Heusler $L2_1$ phase with the space group Fm–3m and $Ni_5Mn_4Ge_3$ impurity phase. $Ni_5Mn_4Ge_3$ is reported to crystallize in hexagonal $P6_3/mmc$ space group [10]. Lattice parameters from the Le Bail fit were obtained as $a = 5.8224(4)$ Å for the cubic Ni_2MnGe phase and $a = 4.9288(9)$ Å and $c = 7.680(3)$ Å for the $Ni_5Mn_4Ge_3$ phase, respectively. Upon further annealing at 950 °C for 4 days, $Ni_5Mn_4Ge_3$ peaks lose their intensity (shown in the inset of Fig. 1), however a pure Ni_2MnGe phase cannot be obtained.

In Fig. 2(a), Backscattered Electron (BSD) image of Ni_2MnGe alloy is shown. There are thin dark regions within the lightly colored matrix. Point analysis from dark regions show a stoichiometry close to $Ni_5Mn_4Ge_3$ in agreement with the XRD data. Neighbouring lightly colored regions show stoichiometric Ni_2MnGe composition (Table 1).

Le Bail fit of the X-ray diffraction data of $Ni_{2.1}Mn_{0.9}Ge$ annealed at 900 °C shown in Fig. 3 can be indexed using a mixture of $L2_1$ Ni_2MnGe Heusler phase together with $Mn_6Ni_{16}Ge_7$. $Mn_6Ni_{16}Ge_7$ phase is cubic with the space group Fm–3m [10]. Refined lattice parameters were $a = 5.7881(5)$ Å and $a = 11.4164(6)$ Å for Ni_2MnGe and $Mn_6Ni_{16}Ge_7$, respectively. Further annealing at 950 °C does not change the stability of the phases.

In Fig. 2(b), BSD image of $Ni_{2.1}Mn_{0.9}Ge$ alloy is shown. Unlike the case in Ni_2MnGe composition, no dark and lightly colored regions could be observed, therefore the presence of a second phase with $Mn_6Ni_{16}Ge_7$ stoichiometry could not be verified. On the other hand, elemental analysis from a large area showed that the target composition has been obtained (Table 1).

In Fig. 4, we show the temperature dependence of magnetization of Ni_2MnGe, $Ni_{2.1}Mn_{0.9}Ge$ and $Ni_5Mn_4Ge_3$ samples measured at 50 Oe. Sharp increase in magnetization in both FC and FH modes define the ferromagnetic Curie temperature as 300 K for Ni_2MnGe and 320 K for $Ni_{2.1}Mn_{0.9}Ge$. There is divergence between FC and FH modes, hinting the possibility of the presence of a first order martensitic phase transition. In order to quantify the contribution of $Ni_5Mn_4Ge_3$ impurity to the magnetic behavior of Ni_2MnGe, a

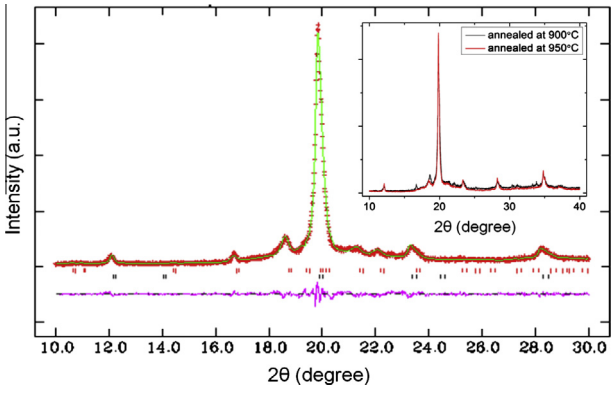

Fig. 1. X-ray diffraction pattern of Ni_2MnGe sample annealed at 900 °C for 3 days. Black ticks denote $L2_1$ Heusler peaks whereas red ticks show $Ni_5Mn_4Ge_3$ impurity phase. Observed data is red, calculated is in green and the difference is in pink. The inset shows a comparison of the diffraction patterns corresponding to the sample annealed at 900 °C and subsequently at 950 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

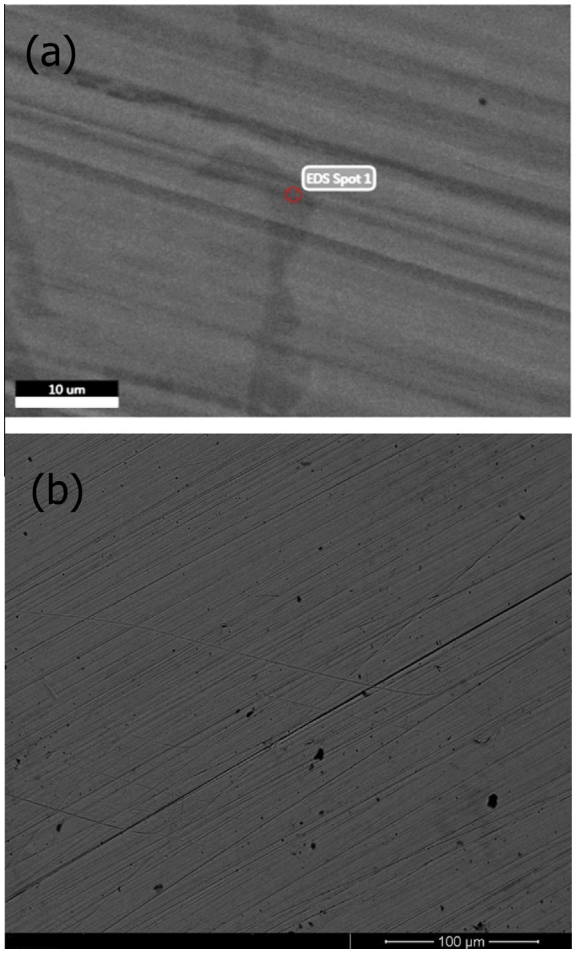

Fig. 2. Backscattered Electron (BSD) SEM images of (a) Ni_2MnGe alloy, annealed at 900 °C for 3 days. Figure shows a zoomed-in region where dark colored $Ni_5Mn_4Ge_3$ phase can be seen, surrounded by the lighter colored regions of Ni_2MnGe phase, (b) $Ni_{2.1}Mn_{0.9}Ge$ alloy, annealed at 900 °C for 3 days. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)