Magnetic, phase transformation and magnetocaloric studies in ferromagnetic Ni$_{55}$Mn$_{20}$Ga$_{25}$ Heusler alloy

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Abstract. The phase transformation and magnetic entropy change ($\Delta S_M$) in the Ni$_{55}$Mn$_{20}$Ga$_{25}$ Heusler alloy has been studied. The temperature dependence of magnetization study shows the direct transition from ferromagnetic martensitic phase to paramagnetic austenitic phase occurred at 353 K. By compositional tuning the first order martensitic transformation ($T_M \sim 200$ K for parent compound Ni$_2$MnGa) and second order magnetic phase transition temperatures ($T_C \sim 375$ K for parent compound Ni$_3$MnGa) can be merged. This occurs for Ni$_{55}$Mn$_{20}$Ga$_{25}$ alloy at 353 K. The magnetic entropy change, $\Delta S_M$-value of -7.0 J kg$^{-1}$ K$^{-1}$ has been obtained in a field change of 1.2 T. The origin of enhancement in $\Delta S_M$-value is attributed to the essential coincidence of $T_M$ and $T_C$.

1. Introduction

Recently interest in magnetocaloric technology has grown significantly due to the development of new magnetic materials such as Gd-Si-Ge, Mn-Fe-P-As, Ni-Mn-Ga, La-(Fe-Si) etc. that exhibit large magnetocaloric (MC) effect near room temperature [1-10]. In the above series of MC materials the ferromagnetic Ni-Mn-Ga Heusler alloys have attracted considerable attention for the application of magnetic refrigeration. In a broad composition range the Ni-Mn-Ga alloys undergo martensitic transition from a cubic (austenite) to tetragonal/orthorhombic/monoclinic (martensite) phase [11, 12]. In both these phases, the magnetic coupling is ferromagnetic however with different ferromagnetic exchange. The difference between the two crystalline structures at low and high temperatures bring about the fundamental difference in their magnetic behavior, causing an abrupt change of magnetization in presence of magnetic field which results in MC effect (MCE). A large $\Delta S_M$ is reported in Gd$_3$Si$_2$Ge$_2$ alloy, in which the structural and magnetic transitions occur simultaneously. In the case of Ni-Mn-Ga alloy, the magnetostructural transformation is very sensitive to the composition and needs fine tuning to occur them simultaneously near to room temperature. By altering the stoichiometry of Ni$_{50}$Mn$_{25}$Ga$_{25}$ Heusler alloy towards Ni rich composition (such that in a series of Ni$_{50-x}$Mn$_{25}$Ga$_{25}$ alloys), $T_M$ and $T_C$ can be tuned to occur simultaneously at $\geq 300$K. $\Delta S_M$ as large as -20.7 J kg$^{-1}$ K$^{-1}$ at 333 K for the field change of 1.8 T has been reported by Chernechukin et al. [10] in Ni-Mn-Ga alloys. The Ni-Mn-Ga alloys have other advantages over Gd$_3$Si$_2$Ge$_2$ and other MC materials such as MnAs$_{1-x}$Sb [11, 13], perovskite manganese oxides [10], or rare-earth based compounds [1, 2]. They are biocompatible, easier to synthesize or fabricate in specific shape (ductile in comparison to the oxides), and less expensive, especially in comparison to the rare-earth or As (highly toxic) containing compounds. In this work, an attempt is made to improve the $\Delta S_M$-value by
tuning the $T_M$ and $T_C$. The evolution of microstructural features, magneto-structural transformation, and magnetic properties are presented in this paper.

2. Experimental Details

The Ni$_{55}$Mn$_{20}$Ga$_{25}$ alloy was prepared by vacuum arc-melting technique of high purity Ni, Mn and Ga as starting elements (99.99% purity). The alloy recovered after each melting batch reverted and remelted (four times) to ensure chemical homogeneity of the alloy. The chemical composition of the alloy was determined using atomic absorption spectroscopy. In addition, electron probe microanalysis was performed for confirming the alloy chemistry. The crystalline structure of the alloys was analyzed with X-ray diffractograms (XRD) using a Philips model-P.W. 1710. The microstructure was studied using a scanning electron microscope (SEM) of JEOL model 35C. Magnetic properties were measured with a DMS-1600 model vibrating sample magnetometer with a maximum field up to 12 kOe. Thermomagnetic measurement was carried out at a biased field of 500 Oe in order to determine the $T_M$ and $T_C$ values. The data was collected during heating cycle at a rate of 10 K/min and the temperature was controlled within an accuracy of ±1 K. Isothermal magnetization curves has been carried out in the magneto-structural transformation region. A TA instrument Q100 differential scanning calorimeter (DSC) was used to monitor heat-flow during the two kinds of the transitions. The data were collected during the heating as well as the cooling cycles at a given 20 K/min rate. A hysteresis of the thermogram occurs in the two cycles is characteristic of thermochemistry of the sample for MC effects of interest in this work.

3. Results and discussion

3.1 Phase transformation and crystal structure

Analysis of XRD patterns reveals that the alloy has a nearly single phase with no detectable secondary phases (Figure 1). The rietveld refinement of the diffracted intensities suggests a tetragonal I4/mmm symmetric structure with $a = 3.881$ Å and $c = 6.502$ Å. Ni atoms occupy 4$d$ (0, 0.5, 0.25) positions, while Mn and Ga atoms occupy 2$b$ (0, 0, 0.5) and 2$a$ (0, 0, 0) positions, respectively. Wedel et al [14] reported the same structure in their work from XRD. Microstructure of the alloy was studied by both optical and scanning electron microscopy techniques. Typical SEM backscattered electron image of the alloy was shown in Figure 2. The alloy exhibits plate like martensite structure at equal spacing. Martensite twins (stripes) are found randomly oriented. Thus, a common implication of the SEM and XRD two independent studies show the presence of martensite phase at room temperature for Ni$_{55}$Mn$_{20}$Ga$_{25}$ alloy.

![Figure 1. The observed (circle symbol) and calculated (red line) X-ray diffraction patterns of Ni$_{55}$Mn$_{20}$Ga$_{25}$ alloy.](image1)

![Figure 2. SEM micrograph showing the presence of martensite strips in Ni$_{55}$Mn$_{20}$Ga$_{25}$ alloy.](image2)
3.2 Structural, Magnetic and magnetocaloric properties

The structural and magnetic transition temperatures of the alloy have been determined from the thermomagnetic (M-T) measurements carried out at the bias field of 500 Oe (Figure 3). The alloy exhibits only a single transition for which T_c is ~353 K. It indicates that the mixed ferromagnetic martensite and ferromagnetic austenite transformed into the paramagnetic austenite at the magnetic transition temperature. The DSC experiment has been carried out in order to observe the T_M-value which is not observed from the M-T curve. T_M-value has been calculated from [1/2 (M_s + A_f)] and is ~352 K where M_s and A_f are the martensite start and austenite finish temperatures respectively. From M-T curve and DCS experiment it has been seen that Ni_{55}Mn_{20}Ga_{25} alloy T_M and T_c values merged with each other. The $\Delta S_M$ is an important parameter to quantify the MCE of a material. It is believed that a large $\Delta S_M$ value arises if the values of T_M and T_c occur simultaneously. To obtain $\Delta S_M$ values for this alloy, isothermal magnetization measurements have been carried out. These measurements are studied at different temperatures around the T_M (or T_c) of the material estimated from M-T data, from which the series of isothermal magnetization curves are generated as shown in Figure 4. It can be seen that the magnetization decreases as we increase the temperature in the same magnetic field. Near the T_M a large change in magnetization was observed. It is interesting to note that the initial magnetization curves (below 340 K) are hard to saturate as it exhibits martensitic phase, having a much larger anisotropy field (H_a =0.8 T) than that of austenite phase (H_a = 0.15 T) [11].

The $\Delta S_M$ can be estimated from magnetization isotherms data by the Maxwell relation, namely

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

where T is the temperature and M is the magnetization.

Ni_{55}Mn_{20}Ga_{25} alloy exhibited large $\Delta S_M \sim -7.0$ J/kg K for a magnetic field change of 1.2 T at 332 K.

The alloy exhibits magnetocaloric effect for active magnetic refrigerant applications near room temperature. The origin of $\Delta S_M$ is ascribed to the discontinuous change of magnetization in the vicinities of the first order magnetic phase transition.

Figure 3. Temperature dependence of dc magnetization for Ni_{55}Mn_{20}Ga_{25} alloy.

Figure 4. Family of isothermal magnetization curves for Ni_{55}Mn_{20}Ga_{25} alloy.
Conclusions
The tetragonal martensite phase has been observed at room temperature for Ni_{55}Mn_{20}Ga_{25} alloy. It displays an enhanced MCE with $\Delta S_M = -7.0$ J/kg K in a field of 1.2 T at 332 K. The origin of the $\Delta S_M$ is related to the essential coincidence of structural and magnetic transition temperature i.e. magnetostructural transformation temperature. This co-incidence is achieved through compositional tuning.

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