Tuning of magnetocaloric potential in disordered Ni-Mn-Sn alloy

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Abstract

The Ni$_{50}$Mn$_{36.5}$Sn$_{13.5}$ alloy was prepared and annealed for four different times (6, 12, 18 and 24 hrs) at 1173 K. The width of the martensitic transition (MT) was found to decrease with the increase of annealing time. The 24 hrs annealed sample showed a larger magnetic entropy change ($\Delta S_M$) near MT, but relatively narrower transition width limited its refrigerant capacity (RC) to a significant extent. The sample annealed for 12 hrs exhibited larger RC and indicated that the partially disordered Ni-Mn-Sn alloys can be a better magnetocaloric candidate as compared to the ordered one.

Keywords: Heusler alloys; Magneto-structural transition; Structural disorder; Magnetocaloric effect; Refrigerant capacity.

1. Introduction

Ni-Mn based Heusler alloys are found to be good magnetic applicant because, they show some multifunctional properties like magnetocaloric effect (MCE) (Planes et al. (2009); Liu et al. (2012); Han et al. (2008); Basso et al. (2012)), magnetoresistance (MR) (Xuan et al. (2008); Ito et al. (2008); Ghosh et al. (2013)), exchange bias (EB) (Xuan et al. (2010); Wang et al. (2012) Giri et al. (2007)), magnetothermal conductivity (MC) (Zang et al. (2007); Kuo et al. (2005); Chandra et al. (2010)), etc. Stoichiometric Ni-Mn based Heusler alloys have cubic ($L_2_1$) structure with four interpenetrating face centered cubic (fcc) sublattices with the formula, Ni$_2$Mn$_Z$ ($Z =$ Ga, Al, Sn, In, Sb) (Ayuela et al. (1999); Helmboldt et al. (1987)). If the structure is completely ordered, Ni atoms takes (0,0,0) and ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$) sites and the remaining ($\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$) and ($\frac{1}{4}$,$\frac{1}{4}$,$\frac{3}{4}$) sites are occupied separately by the Mn and Z atoms. In the case of off-stoichiometric same alloys, the excess Mn atoms occupy the partly vacant $Z$ site. In practical cases, a

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degree of disorder always presents in these alloys where some % of Ni, Mn and Sn atoms occupy the four sites randomly (Sa´nchez-Alarcos et al. (2007)). People use to anneal the as cast sample in high temperatures for a long time to minimize such disorder (Li et al. (2006)). Sokolovskiy et al. (2012) have theoretically studied the Ni-Mn-Sn alloys by intermixing the Mn and Sn atoms in their sublattices. They predict that the density of states and magnetic properties of these alloys change considerably due to both the chemical and structural disorder. A good agreement has been found for the ferro-para Curie temperature \( T_C \) from their calculations and the reported experimental values of these alloys. Thus, a noticeable change in the magnetic and structural properties of the same materials is expected to observe if their disorder can be tuned by some parameter.

The Ni-Mn-Sn off-stoichiometric Heusler alloys have been investigated by many researchers and they have reported large magnetic entropy change \( \Delta S_M \) and refrigerant capacity (RC). The aforementioned properties of these materials generally depend on the first order magneto-structural transition (FOMST) of them (Muthu et al. (2010); Jing et al. (2009); Ghosh et al. (2013); Krenke et al. (2007); Krenke et al. (2005); Ito et al. (2008); ). The constituents’ concentration dependent transition temperatures and \( \Delta S_M \) (Muthu et al. (2010); Ghosh et al. (2013)), substitution of the elements by suitable substitutes (Krenke et al. (2007); Shamberger et al. (2009)) and heat treatment at different temperatures (Shamberger et al. (2009); Ghosh et al. (2013)) have already been reported. But, the change in the magnetic and magnetocaloric properties of these alloys with the change in atomic ordering still needs some investigation (Sokolovskiy et al. (2012)). In this work, we have prepared the Ni_{50}Mn_{36.5}Sn_{13.5} alloy by varying the annealing time in order to attain different levels of structural disorder and studied their magnetocaloric potentials \( \Delta S_M \) and RC. The \( \Delta S_M \) is found to be the maximum for 24 hrs annealed sample but, the sample that annealed for 12 hrs shows the largest net RC as compared to others.

2. Experimental

The Ni_{50}Mn_{36.5}Sn_{13.5} alloy has been prepared by the arc melting technique under a 4N purity Argon atmosphere. The as prepared sample is cut into five pieces and four of them have been annealed separately for different individual times (6, 12, 18 and 24 hrs) at 1173 K. The annealed ampoules are quenched in ice water. The nominal compositions of the prepared samples are confirmed by energy-dispersive spectroscopy (EDS). X-ray diffraction patterns have been carried out using CuK\(_a\) radiation in order to determine the crystallographic parent phase. Magnetic measurements are performed using a vibrating sample magnetometer (Lake Shore, model-7144) up to a field of 1.5 T.

![Fig. 1: XRD patterns of (a) sample A, (b) sample C and (c) sample E at 295 K.](image-url)
3. Results and discussion

The names of the samples that have been annealed separately for different times are named and given in table 1. The XRD patterns for these samples at 295 K (as shown in Fig. 1(a-c)) confirm that the annealed samples are in the austenite phase. In the case of cast alloy (sample A), the crystallographic phase is mixed martensite-austenite. It is found that the highly ordered austenite phase becomes predominant as the samples are annealed for more times (appearance of superlattice diffraction peaks (A(111)) in the XRD pattern of sample E) (Muthu et al. (2010)).

![Fig. 2: Temperature dependence of magnetization (M-T curves) for (a) sample A, (b) sample C and (c) sample E in the presence of 0.1 kOe field.](image)

Fig. 2(a), 2(b) and 2(c) show the temperature dependence of magnetization (M-T curves) for sample A, C and E respectively, in the presence of 0.1 kOe field. A martensite to austenite phase transition can be observed from the zero field cooled (ZFC) curves of these alloys within 270 K to 300 K, where the magnetization is found to increase enormously with the increase of temperature. The field cooled (FC) curves of the same samples show the reverse phase transition. The characteristic temperatures for the structural phase transition: austenite start \((A_S)\), finish \((A_f)\), martensite start \((M_S)\), finish \((M_f)\) are indicated in the M-T curves. The martensite-austenite transition \((T_A = (A_S + A_f)/2)\) and austenite-martensite transition \((T_M = (M_S + M_f)/2)\) are given in table 1. In the temperatures between 300 K and 325 K, a sharp change in magnetization is found from the M-T curves of these samples which is due to a ferro-para transition at the Curie temperature of the austenite phase \((T_{CA})\). The thermal hysteresis \((\Delta T_{th} = T_A - T_M)\) is found to become narrower and the transition width at FOMST \((\Delta T = A_f - A_S)\) becomes sharper with the increase of the duration of annealing. This might be due to the increase in atomic ordering because of annealing. A magnetically inhomogeneous phase may presents in these alloys below 200 K and it is a possible indication of exchange bias (EB). EB originates from the interfacial exchange interaction between the spins of ferromagnetic (FM) and

| Annealing time (hrs) | Samples’ name | \(T_A\) (K) | \(T_M\) (K) | \(\Delta T_{th}\) (K) | \(\Delta T\) (K) | \(T_{CA}\) (K) |
|---------------------|---------------|-------------|-------------|----------------------|----------------|----------------|
| 0                   | A             | 292         | 278         | 15                   | 24             | 310            |
| 6                   | B             | 289         | 276         | 13                   | 23             | 312            |
| 12                  | C             | 287         | 275         | 12                   | 22             | 316            |
| 18                  | D             | 284         | 272         | 12                   | 16             | 319            |
| 24                  | E             | 282         | 271         | 11                   | 12             | 320            |
antiferromagnetic (AFM) layers (Xuan et al. (2009); Wang et al. (2012); Ghosh et al. (2013)). The step like nature in the ZFC \( M-T \) curves is found to increase with the increase of annealing time.

![Fig. 3: M-H curves for (a) sample A, (b) sample C and (c) sample E in the vicinity of martensite-austenite phase transition.](image)

Fig. 3: \( M-H \) curves for (a) sample A, (b) sample C and (c) sample E in the vicinity of martensite-austenite phase transition.

The magnetization vs magnetic field data \( (M-H) \) curves have been plotted in Fig. 3(a), 3(b) and 3(c) for sample A, C and E respectively, within the temperatures between their \( A_S \) and \( A_f \). The saturation magnetization \( (M_{sat}) \) in the ferromagnetic austenite phase is the maximum for the sample E. The \( M-H \) curve at 276 K for the sample E is weakly magnetic like. The heat treatment process affects the magnetic properties of both the structural phases. The FM/AFM correlations are present in these alloy systems. The magnetic ordering between the inter site Mn atoms is FM in the austenite phase and AFM in the martensite phase. Annealing causes an increase in ordering of the Mn atoms to their respective sites, which in turn increase the FM/AFM correlations in these alloy systems (Aksoy et al. (2009)).

![Fig. 4: (a) \( \Delta S_M \) as a function of temperature for sample A, sample C and sample E due to 15 kOe field change. (b) The annealing time dependence of \( \Delta S_M \) and RC for Ni_{50}Mn_{36.5}Sn_{13.5} alloy under the same field change.](image)

Fig. 4: (a) \( \Delta S_M \) as a function of temperature for sample A, sample C and sample E due to 15 kOe field change. (b) The annealing time dependence of \( \Delta S_M \) and RC for Ni_{50}Mn_{36.5}Sn_{13.5} alloy under the same field change.
The $\Delta S_M$ of all the samples has been calculated using Maxwell’s thermodynamic relation (Ghosh et al. (2013))

$$\Delta S_M(T, \Delta H) = \mu_0 \int_0^\infty \left( \frac{\partial M}{\partial T} \right) dH$$

(1)

where, $T$, $M$, $H$ and $\mu_0$ are respectively the temperature, magnetization, magnetic field intensity and permeability of free space. Fig. 4(a) represents the temperature dependence of $\Delta S_M$ for samples A, C and E. The peaks of the $\Delta S_M$-T curves are found to shift in lower temperatures for sample A to E. A maximum $\Delta S_M \sim 5.15$ J/kg K is obtained from the sample E at 285 K under 15 kOe field changes. This larger value of $\Delta S_M$ for the sample E originates from the sharp change in magnetization during the structural phase transition. We have also calculated the RC of these materials from the $\Delta S_M$-T curve using the formula

$$RC = \int_{T_1}^{T_2} |\Delta S_M(T, \Delta H)| dT$$

(2)

where, $T_1$ and $T_2$ are respectively the lower and upper temperatures of the full width at half maxima (FWHM) of $\Delta S_M$-T peak (Ghosh et al. (2013)). RC estimates the total amount of thermal energy that can be transferred to a hot sink ($T_2$) from a cold source ($T_1$) in one ideal thermodynamic cycle. Although, the value of $\Delta S_M$ for sample E is the maximum, the RC is the highest for sample C among them (42 J/kg). The average hysteresis losses due to the field induced hysteresis has been deducted from the RC values and as a result, a net RC $\sim 35.5$ J/kg is obtained from the sample C. Fig. 4(b) shows the dependence of $\Delta S_M$ and net RC of Ni$_{50}$Mn$_{36.5}$Sn$_{13.5}$ alloy on the annealing time. It can easily be noticed that the $\Delta S_M$ increases in a nonlinear way with the increase of annealing time and nearly saturates after 18 hrs but, the net RC has a peak value at the annealing time of 12 hrs and it decreases on the both sides of increasing and decreasing the duration of annealing. For a good magnetocaloric material, the value of $\Delta S_M$ should be high and its corresponding temperature dependent peak should be broad enough so that the same material can be used within a wide temperature range and can extract large amount of heat from the region that needs to cool. In sample C, these aforementioned properties present with satisfactorily larger values as compared to the others and thus predict that disordered Heusler alloys can also be a good magnetic refrigerant.

4. Conclusion

In conclusion, the magnetic and magnetocaloric properties of off-stoichiometric Ni-Mn-Sn Heusler alloy have been investigated systematically by varying the duration of annealing of a single material. The magnetic entropy change is the maximum for the sample that has been annealed for the maximum time. But, the refrigerant capacity of the 12 hrs annealed sample is the maximum among the others. It is evident from our study that up to a certain degree of disorder is required to make Heusler alloys a better magnetic refrigerant.

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