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Large inverse magnetocaloric effect and magnetoresistance in nickel rich $Ni_{52}Mn_{34}Sn_{14}$ Heusler alloy

D. Pal [a,b,*], A. Ghosh [a], K. Mandal [a]

[a] S.N. Bose National Center for Basic Sciences, Block-JD, Sector-III, Salt Lake, Kolkata 700098, West Bengal, India
[b] Kandi Raj College, Kandi 742137, West Bengal, India

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ABSTRACT

Nickel rich $Ni_{52}Mn_{34}Sn_{14}$ Heusler alloy was prepared by arc melting and subsequent homogenization by annealing. Existence of first order magneto-structural transition (FOMST) was confirmed by various measurements. In comparison to conventional $Ni_{50-x}Mn_{36+x}Sn_{14}$ alloys, a larger magnetic entropy change ($\Delta S_M \approx 8$ J/kg K using Maxwell's thermodynamic equation and $\Delta S_M \approx 18$ J/kg K using Clasius–Clapeyron equation) and large negative magnetoresistance (MR $\approx -30\%$) were observed in the vicinity of martensitic transition temperature due to a change of 3 T and 8 T magnetic fields respectively. Effect of excess Ni content was discussed by considering other nearer compositions as reported by other researchers. Irreversibility in FOMST due to kinetic arrest was also studied from MR vs magnetic fields curves taken at a single temperature in two different initial phases. The exchange bias behavior in this alloy was studied by various magnetic measurements.

1. Introduction

Study of ferromagnetic shape memory alloys (FSMA) have attracted immense attention during last decade due to their multi-functional properties such as magnetic shape memory effect [1], large magnetocaloric effect (MCE) [2,3], giant magnetoresistance [4,5], etc. The alloys with composition Gd–Si–Ge, Ni–Mn–Z (Z=Ga, Al, In, Sn, Sb), La–Fe–Si and Mn–Fe–P–As are very useful in this field of study [1–8]. Among the FSMAs, off-stoichiometric composition of Ni–Mn–Z (Z=Ga, In, Sn, Sb) Heusler alloys are the most studied magnetocaloric materials as they show large magnetic entropy change due to magnetic and magneto-structural transitions [9]. In addition to large inverse MCE some of these alloys show large MR near the structural transition temperature on application of high magnetic field [10].

It is remarkable that most of the functional properties of these alloys are associated with the magneto-structural transition from high temperature austenite to energetically favorable low temperature martensite phase [1–5]. The structural instability associated with the field-induced first order structural transition in these alloys can be tuned by varying composition or by substituting suitable atoms in the place of Ni, Mn or Z atoms. In stoichiometric Heusler structure, Ni atoms occupy the octahedral (0, 0, 0) and (1/2, 1/2, 1/2) sites. Mn and Sn atoms occupy the (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4) tetrahedral sites respectively [11]. In case of off-stoichiometric Mn rich Heusler alloys, excess Mn atoms occupy the regular Ni, Sn or both Ni and Sn sites depending on the compositions. These excess Mn atoms in the Ni sites behave ferromagnetically, which lowers the martensitic transition temperature (T_M), but Mn atoms in the Sn sites couple antiferromagnetically to the nearest Mn atoms in the regular Mn sites. This in turn shifts the structural transition to the higher temperatures. As the slope of the structural transition becomes sharper, MCE and magnetoresistance increase abruptly. Till to date many work on magnetocaloric effect, magnetoresistance and exchange bias by varying Ni/Mn, Ni/Z or Mn/Z concentrations have been done by many researchers [2–5]. On the other hand there are many reports in the literature where partial substitution of Co in Ni site and Ga, Si or Ge in Z site enhanced the magnetic entropy change (ΔS_M) to giant values in Ni–Mn–Z alloys [12]. Maximum ΔS_M in substituted Ni–Mn–In, Ni–Mn–Sb and Ni–Mn–Sn alloys was reported 124 J/kg.K, 70 J/kg K and 35 J/kg K respectively under 5 T magnetic fields [13]. Giant magnetoresistance about 80% in the vicinity of magneto-structural transition has also been observed in many Heusler alloys [14]. All these alloys exhibit more or less thermal hysteresis, which corresponds to energy consumption.

Large exchange bias (EB) behavior can be seen in these alloys in low temperature martensite phase. Depending on the nature of magnetic domains, ferro-antiferro (FM–AFM) or super

* Corresponding author at: S. N. Bose National Center for Basic Sciences, Block-JD, Sector-III, Salt Lake, Kolkata 700098, West Bengal, India. Tel.: +91 9475567609.
E-mail address: deba.phy@gmail.com (D. Pal).

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para–antiferro (SPM-AFM) coupling occurs below Neel temperature (T_N). Field cooled (FC) protocol are used to observe spontaneous EB, but recent studies proposed that large EB can also be obtained under zero field cooled (ZFC) condition, from an unmagnetized state of the samples [15,16].

Recently the off-stoichiometric Ni–Mn–Z alloys (near to $Ni_{52}Mn_{48-x}Z_x$) have attracted special attention due to their potential for technical applications such as magnetic refrigeration, magnetic sensor etc. It is reported that in $Ni_{52}Mn_{31.5}In_{16.5}$ alloy the lower Mn atoms in the In atom sites weaken the total AFM interaction, which enhance the entropy change [17]. Whereas for the composition $Ni_{50}Mn_{36.5}In_{13.5,}$ the change of entropy is lower compare to previous one because of paramagnetic martensitic to paramagnetic austenite phase transition [18]. Some researchers have reported large magnetic entropy change and small thermal hysteresis on the Heusler alloys where the component of Ni is larger than 50 at%, such as $Ni_{51}Mn_{49-x}In_x$ [19]. The excess Ni increases the ferromagnetic exchange interaction in these systems and can thus change magnetic and magneto-transport properties of these alloys to a significant extent [17,19]. Therefore, it might be desirable to study Ni-rich Ni–Mn–Sn alloys also.

In our earlier work we have studied magnetocaloric and magneto-transport properties of Ni–Mn–Ga alloys [4,9]. Here we report a large inverse magnetocaloric effect (IMCE) and large negative MR in nickel rich $Ni_{52}Mn_{34}Sn_{14}$ Heusler alloy in the vicinity of its magneto-structural transition. The quantitative values of IMCE and MR are quite higher than the conventional $Ni_{50}Mn_{36}Sn_{14}$ alloy. Existence of kinetic arrest and EB are also investigated for this alloy.

2. Experimental procedure

The $Ni_{52}Mn_{34}Sn_{14}$ alloy was prepared by conventional arc melting technique in a 4 N purity Argon atmosphere. The obtained ingot was wrapped with a Ta foil and homogenized in a highly evacuated sealed quartz ampoule at 1173 K. After 24 h of annealing, the ampoule was quenched in ice water. The nominal composition was checked by energy-dispersive spectroscopy (EDS). To characterize the crystallographic phase of the sample X-ray diffraction pattern was carried out using CuK$_\alpha$ radiation as depicted in Fig. 1. At room temperature the sample was found to be completely cubic-austenite phase with lattice parameter 0.59762 nm. The structural transition temperatures were estimated from differential scanning calorimetry (DSC) measurement. Magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer up to 5 T magnetic fields. Magneto-transport measurements were done using standard four-probe techniques in a physical properties measurement system (PPMS) up to 14 T magnetic fields.

3. Results and discussion

3.1. DSC results and thermomagnetic curves in ZFC condition

The inset of Fig. 2 shows the DSC curves during heating and cooling. The sample undergoes martensite-austenite structural transition near 220 K on heating and reverse transition on cooling near 205 K along with ferro-para magnetic transition at T_C=305 K. Magnetization of $Ni_{52}Mn_{34}Sn_{14}$ alloy as a function of temperature was measured from 4 K to 300 K for both heating and cooling in ZFC condition in the presence of 0.01 T magnetic field and plotted in Fig. 2. *M* vs *T* curves within the temperature from 200 K to 250 K ensure the existence of martensitic transition as seen from DSC curves. The width of the transition is 15 K. The martensite to austenite transition starts at A_s=220 K and ends at A_f=235 K. The reverse transition begins at M_s=220 K and ends at M_f=205 K. The temperature of austenitic transition is given by, $T_A=(A_s+A_f)/2=227.5$ K and for martensitic transition, $T_M=(M_s+M_f)/2=212.5$ K. As our measurements were performed within the temperature from 4 K to 300 K, we could not found the T_C from *M* vs *T* data.

The martensite–austenite transition temperature of our sample is much lower than the reported value of $Ni_{50}Mn_{36}Sn_{14}$ alloy [20]. This is due to the addition of extra Ni atoms in the regular Mn sites. In off-stoichiometric Heusler structure the Mn atoms in regular Mn site interact anti-ferromagnetically with the excess Mn atoms in the Sn site. This AFM interaction stabilizes the martensite phase to a higher temperature. It is well known that Ni, Co or Fe substitution in Mn site enhances the ferromagnetic exchange interaction and diminishes antiferromagnetic coupling between Mn atoms in regular Mn sites and Mn atoms in Sn sites in the martensite phase, which in turns decreases the T_M. This supports the lower value of martensite-austenite transition temperature in our sample with respect to $Ni_{50}Mn_{36}Sn_{14}$ alloy. However it is believed that the martensitic transition depends on the valance electron concentration (*e*/*a*), but recent reports showed that it actually depends on the hybridization of 3d states of Ni and Mn. Ye et. al. [21] suggested for $Ni_2Mn_{1+x}Sn_{1-x}$ alloys that a strong hybridization exists between Ni 3d states and 3d states of Mn at the non-magnetic Sn site. It is demonstrated that after the

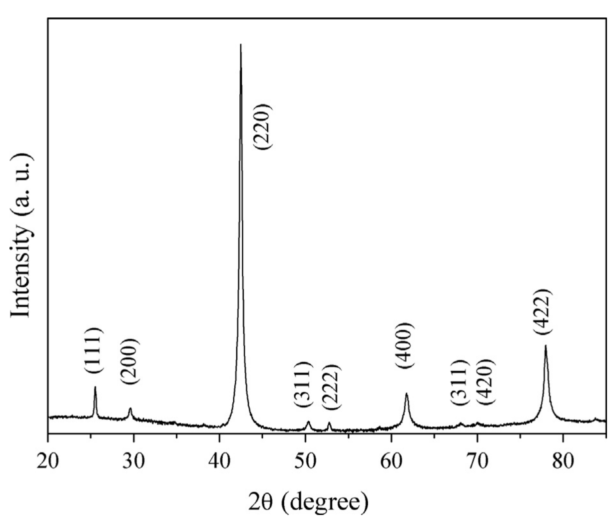

Fig. 1. Powder X-ray diffraction pattern of $Ni_{52}Mn_{34}Sn_{14}$ alloy at room temperature.

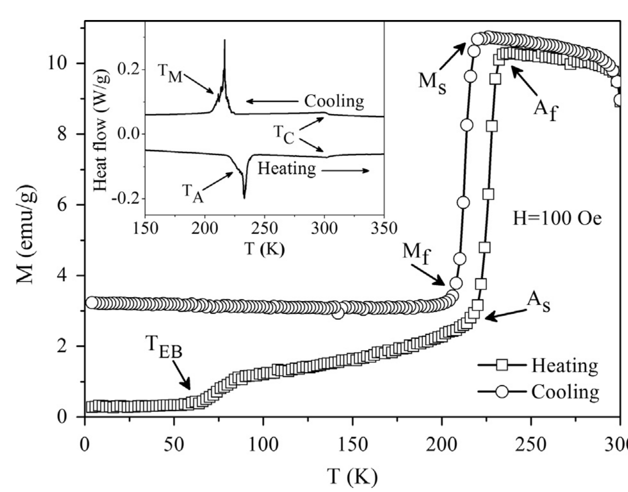

Fig. 2. Thermomagnetic curves in ZFC condition under 100 Oe magnetic fields and DSC curves (inset) for $Ni_{52}Mn_{34}Sn_{14}$ alloy.