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Hydrostatic pressure effects on martensitic transition, magnetic and magnetocaloric effect in Si doped Ni–Mn–Sn Heusler alloys

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ABSTRACT

We report the hydrostatic pressure dependence of martensitic, magnetic and magnetocaloric effect in the $Ni_{48}Mn_{39}Sn_{13-x}Si_x$ ($x = 1$ and 4) Heusler alloys. The martensitic transition temperature increased with respect to pressure at the rate of 2.37 K/kbar and 0.7 K/kbar for $x = 1$ and 4 alloys respectively and decreases with the application of magnetic field at the rate of 1.2 K/T and 0.8 K/T for $x = 1$ and 4 alloys respectively. The Curie temperature of austenite phase changes marginally under pressure. The maximum magnetic entropy change (ΔS_M) of 5.13 J kg^{-1} K^{-1} at 0 kbar and 24.5 J kg^{-1} K^{-1} at 9.7 kbar were observed for $x = 1$ alloy. However the magnetic entropy change for $x = 4$ alloy seems to decrease as a function of pressure.

1. Introduction

The hunt for large magnetocaloric (MC) materials near room temperature has turned into a most interesting topic due to their use in cooling devices where it replaces the conventional gas compression. The materials such as $MnFeP_{1-x}As_x$, $MnAs_{1-x}Sb_x$ and $LaFe_xSi_{1-x}$ are considered as efficient magnetic refrigeration materials for their giant magnetocaloric effect (MCE) around room temperature [1–3]. The MCE property in these materials has been improved by varying the chemical composition and doping different elements into the existing materials. The MCE property can also be tuned by the external factors or suitable quantum critical points such as magnetic field and pressure (hydrostatic or uniaxial). The pressure modifies the magnitude of the MCE in the materials such as $Tb_5Si_2Ge_2$, MnAs and Er_5Si_4 [4–7]. In recent years, the Ni–Mn based alloy system regarded as a promising material for the application in magnetic refrigeration. These Ni–Mn based alloy systems undergo a phase transition from austenite cubic $L2_1$ structure to the martensitic phase, where the magnetization of martensitic phase is noticeably smaller (for Ni–Mn–Ga, magnetization in the martensite phase is higher than the austenite phase) than in the austenite phase [8–10]. The pressure influences the diffusionless martensitic phase transformations that are accompanied by a volume change in these alloys and the magnetic properties depend upon the inter-atomic distance between Mn and Mn atoms. The external pressure can modify the Mn–Mn distance thereby changes the magnetic property. The change in magnetic property by pressure also has subsequent influence in the MCE. Several reports have already been published in the pressure effects on phase transition temperature in Ni–Mn–X (X = Ga, In, Sn) alloys [11–13]. However, there were few reports on the pressure effects on MCE [14–18] and recently the barocaloric effect was reported in Ni–Mn–In alloys [19]. Recently, we have studied the variation of martensite transition and multifunctional properties such as exchange bias and magnetoresistance at ambient pressure in iso electron substituted $Ni_{48}Mn_{39}Sn_{13-x}Si_x$ ($1 \leqslant x \leqslant 4$) Heusler alloys [20]. In this letter we report the influence of hydrostatic pressure on martensitic and magnetic transition, MCE and refrigeration capacity in iso-electron substituted $Ni_{48}Mn_{39}Sn_{13-x}Si_x$ ($x = 1$ and 4) Heusler alloys.

2. Experimental techniques

Ingots of $Ni_{48}Mn_{39}Sn_{13-x}Si_x$ ($x = 1, 4$) alloys were prepared by melting high purity starting elements (99.9% pure) using an arc melting furnace under argon atmosphere. The samples are re-melted four times to ensure homogeneity. The alloys are annealed under high vacuum at 1175 K for 6 h and then quenched with Ar gas. Elemental composition of these alloys were determined using scanning electron microscopy (SEM, Leo 440i) attached with an X-ray energy dispersive spectroscope (EDS) setup and are found to be close to the nominal composition. The structural

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analysis are carried out by cooling the sample in a CCR type cryostat attached to powder X-ray diffractometer (XRD) instrument fitted on a rotating anode X-ray generator. XRD pattern was recorded in step-scan mode (in steps of 0.02°) using Cu Kα. The magnetization measurements were performed at various pressure by means of a Physical Property Measurement System (PPMS-9T) - Vibrating Sample Magnetometer (VSM) module equipped with the Cu–Be clamp type pressure cell with a maximum pressure of 10 kbar (Quantum Design, USA). The thermomagnetic data was recorded upon field cooling (FC) and field warming (FW) with an applied field of 10 mT in the temperature range between 330–100 K. Magnetization as a function of magnetic field was recorded up to a field of 9 T for various pressures.

3. Results and discussion

3.1. Structural studies

The room temperature powder XRD pattern for $x = 1$ and 4 alloys reveals that the alloys contain Heusler $L2_1$ structure with the space group of $Fm\bar{3}m$ [20]. Further the low temperature powder XRD pattern for $x = 4$ alloy at 125 K was recorded and shown in Fig. 1 and the inset shows the clear view of maximum intensity peaks. The recorded data was fitted with LeBail method using FULLPROF software package [21,22]. The XRD peaks are indexed by monoclinic cell. The lattice parameters obtained for 125 K are $a = 4.338$ Å, $b = 5.57$ Å, $c = 30.01$ Å with a space group of $P\ 2/m$. The ratio $c/a \sim 7a$ indicates the seven layered (7M) modulation in $x = 4$ alloy. This confirms the structural change from cubic austenite phase to 7M modulated monoclinic martensite phase in the alloy.

3.2. Magnetic studies

Fig. 2(a) and (b) shows the temperature dependence of magnetization $M(T)$ in an applied magnetic field of 10 mT with different hydrostatic pressures (P) for $Ni_{49}Mn_{38}Sn_{13-x}Si_x$ ($x = 1$ and 4) alloys. It can be seen from Fig. 2 that the second order phase transition from paramagnetic to ferromagnetic austenite (T_C) occurs at high temperature region with increase in magnetization (M) for $x = 1$ alloy at ambient pressure. The observed hysteresis between FC and FW is an indication of first order structural transition from austenite to martensite phase. The application of external hydrostatic pressures (1.6, 7.3 and 9.7 kbar) shifts the structural transition temperatures (STT) martensitic start (M_s) and finish (M_f), austenite start (A_s) and finish (A_f) towards the higher temperature value. Similar behaviour is also observed in the pressure dependence of $M(T)$ curve for $x = 4$ alloy as shown in Fig. 2(b). The magnitude of M in $M(T)$ curve increase (decrease) as we increase the pressure for $x = 1$ ($x = 4$) alloy. It is clear from Fig. 2 that no appreciable change in the width of hysteresis is observed as we increase the pressure for both the alloys. The pressure dependence of T_C (=+0.49 K/kbar) is higher for $x = 4$ alloy while comparing with $x = 1$ alloy ($dT_C/dP = +0.2$ K/kbar). It is known that the Mn ($\sim 4\mu_B$) atom possess high magnetic moment comparing to the magnetic moment of Ni ($0.3\mu_B$) atom and the Ni–Mn exchange interaction is nearly pressure independent, while the exchange interaction of Mn–Mn atom increases with pressure [23]. Hence, the positive pressure dependence of T_C in the present alloy is attributed to the change in ferromagnetic interaction of Mn–Mn atoms with pressure.

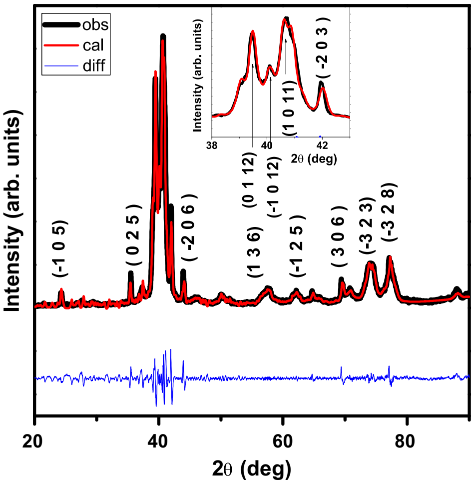

Fig. 1. Powder X-ray diffraction pattern for $x = 4$ alloy measured at 125 K.

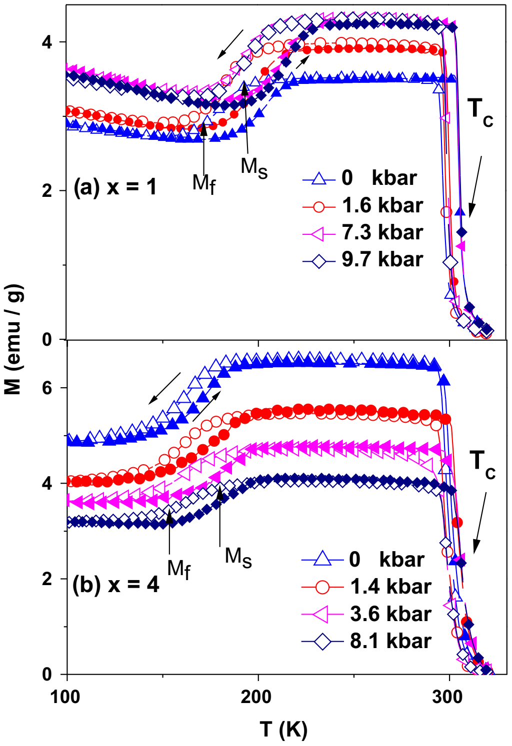

Fig. 2. Thermomagnetic curves for: (a) $Ni_{48}Mn_{39}Sn_{13-x}Si_x$ ($x = 1$) and (b) $Ni_{48}Mn_{39}Sn_{13-x}Si_x$ ($x = 4$) alloys at various applied pressures in an applied bias field of 10 mT. (Open symbol and solid symbols correspond to cooling and warming cycle respectively.)

Fig. 3(a) and (b) shows the pressure dependence of M_s, M_f, A_s and A_f for $x = 1$ and 4 alloys. The martensitic transformation temperature (T_m) is calculated using the equation, $(M_s + M_f + A_s + A_f)/4$. It is found that the STT increases linearly with the application of pressure for both alloys. The pressure derivate of M_s ($dM_s/dP = 2.37$ K/kbar) is higher for $x = 1$ alloy than the $x = 4$ alloy (0.7 K/kbar). The Heusler alloys displaying lower relative volume change at martensitic transition results in smaller shift in M_s temperature [12]. The relative volume change in the martensitic phase under pressure is very low for $x = 4$ alloy than the $x = 1$ alloy. It is observed that at a temperature above T_m, the alloys are in austenite phase while below T_m the alloys are in the martensite phase. The change of the transformation temperature by the pressure can be explained by the Clausius–Clapeyron relation, $dT/dP = \Delta v/\Delta S$, where ΔS and Δv are the change in entropy and volume respectively at the phase transition. Hence, the higher Δv or lower ΔS results in a larger shift in the transformation temperature. The application of pressure would reduce the volume and results in the change in martensitic transition temperature with pressure. The increase of pressure also increases the hybridization between Ni and Mn/Sn bonds. Thus, more thermal energy is required to