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Magnetocaloric Properties of Low-Cost Fe and Sn Substituted MnNiSi-Based Alloys Exhibiting a Magnetostructural Transition Near Room Temperature

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The magnetocaloric properties of rare-earth free $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ ($y = 0.12, 0.14, 0.16, \text{ and } 0.18$) alloys were studied. The raw material cost is significantly lower than the counterpart alloys containing Ge or Ga. Sn substitution reduced the Curie temperature (T_c) from 343 K (for $y = 0.12$) to 248 K (for $y = 0.18$), offering a wide range of working temperatures near room temperature. The alloys exhibited a training effect. The first-order transition weakened as the Sn content increased from 0.12 to 0.18. Interestingly, magnetostructural transformation was observed near room temperature for $y = 0.14$, with a maximum entropy change (ΔS_{max}) of $8.64 \text{ Jkg}^{-1}\text{K}^{-1}$ for a field change of 5 T. Hence, $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ alloys are promising candidates for low cost, near room temperature, magnetocaloric applications.

Index Terms—Magnetic phase transition, magnetocaloric effect (MCE), structural transition.

I. INTRODUCTION

MAGNETOCALORIC effect (MCE)-based thermal management technology is emerging as an attractive energy efficient, green alternative to conventional vapor-compression cooling systems. There is high interest in magnetocaloric cooling due to numerous advantages such as high efficiency [1], no noise, vibration, and no ozone layer depleting gases [1], [2]. Recently, magnetic cooling wine chillers were commercialized by BASF [3], GE [4], Haier [5], and supermarket chiller developed by Cooltech for Carrefour [6]. The MCE is the thermal response of a magnetocaloric material (MCM) to an applied magnetic field. The MCE is greatly enhanced when there is a simultaneous magnetic and structural transition, the so-called magnetostructural transition (MST) [7], [8]. This overlap of the magnetic and structural transitions can be a first-order magnetic transition (FOMT). A tunable magnetostructural transition temperature (T_t) can provide a wide operating temperature range, extending the range of applications [9].

Materials exhibiting FOMT have been of interest in recent years due to their high entropy change, which enhances the MCE. MnTX ($T = \text{Ni, Co}$ and $X = \text{Si, Ge}$) based alloys such as MnNiGe , MnCoGe , and MnNiSi exhibit both a magnetic and a structural transitions, T_t can be tuned by alloying [10]–[12]. Specifically, MnNiSi exhibits a structural transition between a low-temperature orthorhombic phase (TiNiSi-type structure, space group Pnma) and a high-temperature hexagonal phase (Ni_2In -type structure, space group $\text{P6}_3/\text{mmc}$) at 1200 K [11], and a magnetic transition from a ferromagnetic (FM) state to a paramagnetic (PM)

state at 622 K [13]. This wide separation of the magnetic and structural transition temperatures makes it challenging to achieve magnetostructural coupling in MnNiSi . It has also been shown that single-element substitution is insufficient to achieve magnetostructural coupling near room temperature [14]–[16]. Hence, two alloying elements are needed to obtain magnetostructural coupling near room temperature for MnNiSi -based alloys. MST near room temperature occurred in MnNiSi -based systems such as MnNiSi-FeNiGe [17], MnNiSi-FeCoGe [18], MnNiSi-MnFeGe [19], $\text{MnNiSi-Fe}_2\text{Ge}$ [20], [21], MnNiSi-CoNiGe [22], $(\text{Mn, Fe})\text{Ni}(\text{Si, Al})$ [23], $(\text{Mn, Fe})\text{Ni}(\text{Si, Ga})$ [24], and $(\text{MnNiSi})_{1-x}(\text{Co}_2\text{Ge})_x$ [25]. Mn has been substituted by Fe; Co and Si by Al, Ga, and Ge. However, the substitution of Si by low-cost Sn has not been studied. Hence, in this paper, the effect of Sn and Fe alloying additions to MnNiSi on the MST has been investigated.

To achieve enhanced MCE during the magnetostructural transition, the orthorhombic phase must possess a high value of saturation magnetization, which will result in a large difference in magnetization (ΔM) between the FM and the PM phases [26]. The magnetic moment in MnNiSi and MnNiGe alloys is located mainly at the Mn atoms; small changes in the interatomic distance between adjacent Mn atoms can significantly influence the magnetization of the alloy [14]. The interatomic distance between Mn atoms can be varied by introducing substitutional elements that can occupy Mn sites [16]. The magnetic properties of such alloys $\text{MM}'\text{X}$ ($M, M' = \text{transition metal}$) are highly dependent on the nature of the covalent bond between M' and X atoms [27], [28]. Hence, Fe atoms were used to substitute for Mn atoms. Fe substitution for Mn in MnNiSi reduces T_t and T_c more rapidly than Co substitution [16]; therefore, Fe was chosen as the first substitutional element. The substitution of $x = 0.55$ in $\text{Mn}_{1-x}\text{Fe}_x\text{NiSi}$ alloys can reduce T_c to a value of 438 K [16]; therefore, the Fe composition was fixed

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Fig. 1. (a) XRD pattern of arc melted $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ with y varying from 0.12 to 0.18. The hexagonal peaks are dominant in the alloys with $y = 0.18$, whereas orthorhombic peaks are significant for $y = 0.12$. (b) High-temperature XRD for $y = 0.12$ sample from 303 to 423 K, a transition from orthorhombic to hexagonal structure was observed as the temperature was increased.

at 0.55 and Si was substituted by Sn to further reduce T_c to near room temperature values. To produce a low-cost alloy, the starting elements must be inexpensive. Sn is 15 times cheaper than Ge and 10 times cheaper than Ga [29]; hence, the use of Sn will reduce the cost of the alloy. The alloys exhibited the “virgin effect” (also known as training effect) observed for the first 3 heating and cooling cycles. This phenomenon was also reported in other MCE materials with large magnetoelastic coupling, e.g., La-Fe-Si alloys [30], $(\text{Mn}, \text{Fe})_2(\text{P}, \text{Ge})$ [31], $\text{Mn}_{0.53}\text{Fe}_{0.47}\text{NiSi}_{0.53}\text{Ge}_{0.47}$ [32], and Mn-Fe-P-Si [33], [34]. There are no previous magnetocaloric studies of Sn substitution in MnNiSi-based alloys; hence, the MCE of Fe and Sn substituted MnNiSi alloys was also investigated.

II. EXPERIMENTAL PROCEDURE

Nominal compositions of Mn (99%; Sigma Aldrich), Ni (99.8%, Alfa Aesar), Si (99.95%; Sigma Aldrich), Fe (99.98%; Sigma Aldrich), and Sn (99.9%; Alfa Aesar) were arc melted to form alloys of composition $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ with $y = 0.12, 0.14, 0.16$, and 0.18. To compensate the loss of Mn during arc melting, 5% (by weight) additional Mn was taken. The samples were remelted several times in the arc melter to ensure homogeneity. Subsequently, samples were subjected to three heat cycles by placing the sample in liquid nitrogen and subsequently heating them above 350 K to avoid the “virgin effect” in these alloys [35]. Characterization of samples were carried out using X-Ray diffraction (XRD) (Bruker D8) at room temperature, with a step size of 0.018° and Cu-K α radiation, and differential scanning calorimetry (DSC) (Q10 V9.9 Build 303) with a ramp rate of 10 K/min was employed to identify the structural transition. A physical property measurement system (Quantum Design Evercool-II) with vibrating sample magnetometer attachment was used to make magnetic measurements up to 5 T.

III. RESULTS AND DISCUSSION

The XRD patterns of $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ ($y = 0.12$ and 0.18) at room temperature are shown in Fig. 1 (a). It can be observed that there is a mixture of orthorhombic and

Fig. 2. DSC plots for $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ ($y = 0.12, 0.14$, and 0.16) showing the heating and cooling cycles with a ramp rate of 10 K/min.

hexagonal phases in the alloys. For a lower concentration of Sn ($y = 0.12$ and 0.14), the orthorhombic structure dominates. For higher Sn concentration ($y = 0.16$ and 0.18), the hexagonal peaks show higher intensity indicating a dominant hexagonal structure in these alloys. Fig. 1 (b) shows high-temperature XRD patterns, ranging from 303 to 423 K, for the $y = 0.12$ alloys, hexagonal peaks were predominant at higher temperatures (393 and 423 K). On the other hand, orthorhombic peaks were observed at 363, 333, and 303 K, thus there is a change in crystal structure from orthorhombic to hexagonal when the alloy is heated beyond the transition temperature.

DSC analysis was carried out to determine the structural transition temperatures, a ramp rate of 10 K/min for both heating and cooling cycles was employed (Fig. 2). This DSC analysis showed structural transformation peaks at 325, 360, and 382 K in the heating cycle and 260, 305, and 330 K in the cooling cycle for $y = 0.16, 0.14, 0.12$, respectively. A broader peak for $y = 0.16$ indicates a gradual change in the structure with temperature. No peak was observed in the DSC analysis for $y = 0.18$, suggesting that the first-order transformation is limited to Sn compositions below $y = 0.16$. Thus, the substitution of Si by Sn reduces the transformation temperature of $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ alloy.

The arc-melted samples initially showed variation in T_c when subjected to heating and cooling cycles; however, there was negligible variation in T_c after the third cycle. Fig. 3 shows the magnetization versus temperature plots for the first 3 heating and cooling cycles. This virgin effect has also been observed previously in MnAs-based alloys [36], $(\text{Mn}, \text{Fe})_2(\text{P}, \text{Ge})$ [37], [38], $(\text{Mn}, \text{Fe})_2(\text{P}, \text{Si}, \text{Ge})$ [31], [39], $\text{Mn}_{0.53}\text{Fe}_{0.47}\text{NiSi}_{0.53}\text{Ge}_{0.47}$ [32], and MnCoGe-based alloys [40]. It occurs due to the irreversible structural transformation and is related to the presence of a metastable state preserved in the as-prepared sample when it is cooled from high temperature. This metastable phase transforms to the desired low-temperature phase upon repeated heating and cooling cycles. A similar phenomenon was observed in our alloy. When the bulky Sn atoms are forced into the MnNiSi lattice, it increases the energy barrier for transformation between the high-temperature hexagonal and the low-temperature orthorhombic structures during the first cooling

Fig. 3. M versus T plot for $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ ($y = 0.14$) showing the first three heating and cooling cycles. T_c stabilizes after the third cycle.

Fig. 4. (a) M versus T plots for $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ ($y = 0.12$ – 0.18) measured at a constant field of 0.1 T. (b) Moment versus field plot (0–5 T) for $y = 0.12$ for temperatures ranging from 310 to 355 K, measured at 5 K intervals.

cycle due to the elastic strain developed in the lattice. To reduce this strain in the lattice of the virgin alloy, a very large supercooling is required as the driving force. During the subsequent cycles, the strain relaxation in the lattice occurs at a smaller supercooling until the stabilization of the transition temperature during heating and cooling. The existence of structural distortion due to lattice strain results in the local fluctuation of the interatomic distances and the related magnetic exchange interactions. Therefore, during the first cooling, the local fluctuations of the magnetic exchange interaction hinder the structural change around T_c [41]. Once the transition is accomplished after three thermal cycles, the structure will have the opportunity to relax to a more stable configuration under the driving force of magnetic exchange interactions.

The magnetization versus temperature curves were obtained for $y = 0.12, 0.14, 0.16$, and 0.18 compositions at a constant applied field of 0.1 T to obtain stabilized M – T plots after three heating and cooling cycles (Fig. 4). All the alloy compositions showed an FM to PM transition with significant temperature hysteresis. The Curie temperatures of the alloys during heating and cooling cycles are provided in Table I. The increase in Sn content from 0.12 to 0.18 weakens the first-order transition, resulting in a shift of T_c to lower temperature.

TABLE I
CURIE TEMPERATURE OBTAINED FROM M VERSUS T PLOTS DURING HEATING AND COOLING FOR $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ ($y = 0.12$ – 0.18)

Composition (y)	T_c Heating (K)	T_c Cooling (K)	Hysteresis (K)
0.12	355	343	12
0.14	332	312	20
0.16	301	263	38
0.18	275	248	27

In MM' X alloys, the magnetic and structural properties are strongly related to changes in the local chemical bonds [28]. The strength of the covalent bonds formed between M' and X atoms determine the stability of the structure [14]. The structure having higher strength of covalent bonds between atoms is more stable than a structure with lower covalent bond energies between the atoms. Since, Ni and Si have identical electronegativity (χ) of 1.9, whereas Mn has lower χ of 1.55; hence, Ni–Si bonds are preferred compared to Mn–Ni or Mn–Si bonds in MnNiSi alloys [16]. By substitution of Mn and Si atoms by other alloying elements, new bonds can be formed between the alloying element and Mn, Ni, and Si. This trend has been previously observed in the case of replacement of Si by Ge in MnNiSi ($T_f = 1200$ K) to obtain MnNiGe ($T_f = 470$ K), substitutional addition of Al to MnNiGe [10], addition of Fe to MnNiGe [42] replacing 3-D elements such as Fe, MnCoGe in $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ alloys [15] and Co, Fe additions to MnNiSi in $\text{Mn}_{1-x}(\text{Co,Fe})_x\text{NiSi}$ alloys [16].

In the case of Fe and Sn additions to MnNiSi alloys, Sn atoms occupy Si sites, whereas Fe atoms occupy Mn and Ni sites. The bonds formed between Ni–Sn have lower bond energy (180.4 kJ/mol) compared with Ni–Si bonds (318 ± 17 kJ/mol) [43], which lowers the temperature for structural transition. The Fe atoms occupying the Mn sites decrease the length of the c -axis, resulting in a change in Mn–Mn interatomic spacing, which stabilizes the hexagonal structure [44]. The driving force for the structural transformation is related to the vibrational amplitude of the atoms, which increases with temperature [45]. At T_f , the atomic vibration in the orthorhombic structure results in rearranging of atoms to hexagonal structure. As the temperature increases beyond T_f , the PM phase is produced.

The magnetic moment was measured for temperatures in the vicinity of the magnetostructural transition to obtain M – H plots at each temperature. The M – H plot for $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{0.88}\text{Sn}_{0.12}$ is shown in Fig. 4 (b) from 355 to 310 K during cooling. A significant variation of magnetization during increasing and decreasing field was observed, this effect arises due to the constraint of the lattice which prevents the moments from flipping back when the field is reduced.

The M – H measurements were performed using the loop method [46] to avoid spurious peaks during entropy determination. The alloy was exposed to temperatures where it exhibits a PM phase before performing the M – H measurements at each temperature.

Fig. 5. ΔS versus T plots for $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ ($y = 0.12, 0.14, 0.16$, and 0.18) for field change of 2 and 5 T.

TABLE II
 ΔS_{max} VALUES FOR A FIELD CHANGE OF 5 AND 2 T OBTAINED
AT THE TRANSITION TEMPERATURE FOR
 $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ ($y = 0.12-0.18$)

Composition (y)	ΔS_{max} at $\Delta H = 5\text{ T}$ ($\text{J kg}^{-1}\text{K}^{-1}$)	ΔS_{max} at $\Delta H = 2\text{ T}$ ($\text{J kg}^{-1}\text{K}^{-1}$)	Temperature at ΔS_{max} (K)
0.12	7.36	2.96	335
0.14	8.64	3.28	317.5
0.16	3.16	1.15	262.5
0.18	1.35	0.56	155

The entropy change was determined using the Maxwell relation given by the following equation:

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T} \right) dH. \quad (1)$$

The maximum entropy change (ΔS_{max}) for a field change of 2 and 5 T is shown in Fig. 5, the values for ΔS_{max} are shown in Table II.

The values of ΔS_{max} are comparable with those other magnetocaloric alloys, e.g., the benchmark material Gd ($8.3 \text{ J kg}^{-1}\text{K}^{-1}$) [47] and $\text{LaFe}_{10.6}\text{Si}_{2.4}$ ($5.85 \text{ J kg}^{-1}\text{K}^{-1}$) [48]. Although the entropy values are lower than some MnNiSi giant magnetocaloric alloys such as $(\text{MnNiSi})_{0.62}(\text{CoNiGe})_{0.38}$ ($40.3 \text{ J kg}^{-1}\text{K}^{-1}$) [43], $(\text{MnNiSi})_{0.65}(\text{Fe}_2\text{Ge})_{0.34}$ ($57.6 \text{ J kg}^{-1}\text{K}^{-1}$) [21], and $(\text{MnNiSi})_{0.46}(\text{MnFeGe})_{0.54}$ ($40 \text{ J kg}^{-1}\text{K}^{-1}$) [14], the cost of synthesis of $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ is much lower since Sn is much cheaper than that of Ge, Ga, or other rare-earth elements.

The relative cooling power (RCP) is yet another important parameter which determines the effectiveness of MCM. It is the magnitude of heat transferred between hot and cold reservoirs during an ideal refrigeration cycle [49]. The value of RCP can be obtained from the area under the ΔS versus T curve, either by finding the product of full-width at half-maximum (FWHM) and ΔS_{max} value or by integration between the half-maximum limits of the curve.

The RCP values for $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ obtained by product of FWHM and the ΔS_{max} value were 116, 79, 133, and 156 J kg^{-1} for $y = 0.12, 0.14, 0.16$, and 0.18 , respectively. The RCP values are comparable with other MnNiSi-based alloys, e.g., $\text{Mn}_{0.4}\text{Fe}_{0.6}\text{NiSi}_{0.96}\text{Ga}_{0.04}$ (136 J kg^{-1}) [24] and $(\text{MnNiSi})_{0.62}(\text{CoNiGe})_{0.38}$ (169 J kg^{-1}) [43].

Temperature averaged entropy change (TEC) is yet another material-based figure of merit for magnetocaloric alloys [50]. The TEC values were calculated for the temperature range (ΔT_{lift}) of 10 and 3 K. The TEC (10) values for $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ obtained from ΔS versus T plots were 6.06, 6.12, 2.97, and $1.35 \text{ J kg}^{-1}\text{K}^{-1}$, and TEC (3) values were 6.94, 7.88, 3.11, and $1.35 \text{ J kg}^{-1}\text{K}^{-1}$ for $y = 0.12, 0.14, 0.16$, and 0.18 , respectively.

The relatively large temperature hysteresis of $\sim 20 \text{ K}$ would limit the solid-state applications of this alloy when low hysteresis is an important prerequisite for the working material. However, for near room temperature applications requiring low cost, rare-earth free, high entropy, and high RCP alloys, the $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ alloys are highly promising.

IV. CONCLUSION

The MCE of substitutional addition of low-cost Fe and Sn to MnNiSi alloys was studied for the first time. $\text{Mn}_{0.45}\text{Fe}_{0.55}\text{NiSi}_{1-y}\text{Sn}_y$ ($y = 0.12, 0.14, 0.16$, and 0.18) alloys exhibited a first-order magnetostructural phase transition. Increasing the Sn content led to a decrease in T_c from 343 K (for $y = 0.12$) to 248 K (for $y = 0.18$). Thus, a wide Curie temperature window near room temperature was obtained for a range of Sn composition. A magnetostructural transition with ΔS_{max} of $8.64 \text{ J kg}^{-1}\text{K}^{-1}$ was observed for $y = 0.14$ at 317.5 K, and an RCP of 156 J kg^{-1} was obtained for $y = 0.18$. These low cost, rare-earth free alloys exhibiting relatively high entropy change and RCP are promising for near room temperature applications.

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