Microstructure, magnetic and magnetocaloric properties of $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys

Yaoxiang Geng^{1*}, Zhijie Zhang¹, Ojied Tegus², Chuang Dong³ and Yuxin Wang^{1*}

ABSTRACT The present work is devoted to investigating the microstructure, magnetism and magnetocaloric effects of Si- and Mn-rich FeMn(P,Si) alloys. The Mn-substituted alloys with $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ ($x = 1.25, 1.30, 1.35, 1.40, 1.45$ and 1.50) were prepared by high-energy ball milling and solid-state reaction. Experimental results show that the alloys crystallized into a majority Fe_2P -type hexagonal structure, coexisting with minor amounts of $(\text{Mn,Fe})_3\text{Si}$ and $(\text{Mn,Fe})_5\text{Si}_3$ phases. The Curie temperature decreased linearly from 321 to 266 K with increasing Mn content from 1.25 to 1.50 in $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys. The first-order magnetic phase transition became weakened and the second-order magnetic phase transition became dominated with increasing Mn content. $\text{Fe}_{0.75}\text{Mn}_{1.25}\text{P}_{0.4}\text{Si}_{0.6}$ alloy presents a maximum isothermal magnetic-entropy changes of $7.2 \text{ J (kg K)}^{-1}$ in a magnetic field change of 0–1.5 T. The direct measurement shows that $\text{Fe}_{0.7}\text{Mn}_{1.3}\text{P}_{0.4}\text{Si}_{0.6}$ and $\text{Fe}_{0.65}\text{Mn}_{1.35}\text{P}_{0.4}\text{Si}_{0.6}$ alloys exhibit a maximum adiabatic temperature change of 1.8 K in a magnetic field change of 0–1.48 T. The thermal hysteresis for all alloys is less than 4 K. These experimental results reveal that $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys could be a candidate material for magnetic refrigeration.

Keywords: $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys, microstructure, thermal hysteresis, magnetic-entropy change, adiabatic temperature change

INTRODUCTION

This decade has brought an immense interest in room temperature magnetic refrigeration, because it is considered as a type of potential energy saving material and friendly to environment [1–3]. Magnetic refrigeration based on magnetocaloric effect (MCE), is an isothermal magnetic-entropy change ($-\Delta S_m$) or an adiabatic temperature change (ΔT_{ad}) for a magnetic material upon application of a magnetic field [4]. The current investigation of the room temperature MCE mainly focuses on the

first-order magnetic phase transition (FOMT) materials, such as $\text{Gd}_5(\text{Ge}_{1-x}\text{Si}_x)_4$, $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}$ and their related compounds, $\text{MnAs}_{1-x}\text{Sb}_x$, $\text{MnFeP}_{1-x}\text{As}_x$ and MnCoGeB_x [5–10]. These materials exhibit large $-\Delta S_m$ in the vicinity of the magnetic-phase transition from a paramagnetic state to a ferromagnetic state. After the discovery of the giant MCE in MnFe(P,As) , many efforts have been devoted to replacing As by non-toxic components. The introduction of Si and Ge atoms into the lattice of MnFe(P,As) retains a giant MCE around room temperature, but an enhanced thermal hysteresis (ΔT_{hys}) is observed [11,12]. Recently, some meaningful studies have been done to reduce the ΔT_{hys} for MnFe(P,Ge) and MnFe(P,Si) compounds. For $\text{Mn}_{2-y}\text{Fe}_y\text{P}_{0.75}\text{Ge}_{0.25}$ compounds, their ΔT_{hys} can be reduced to 1.0 K by changing the Mn/Fe ratio and maintain a large maximum isothermal magnetic-entropy change ($-\Delta S_{max}$) $\sim 20 \text{ J (kg K)}^{-1}$ in a field change of 0–2 T around room temperature [13]. MnFe(P,Si) compounds also show giant MCE with a large $-\Delta S_{max}$ of $12.8\text{--}18.3 \text{ J (kg K)}^{-1}$ in a field change of 0–2 T and a larger maximum adiabatic temperature change (ΔT_{ad}^{max}) of 2.2 K in a field change of 0–1.1 or 0–1.48 T [14–17]. The ΔT_{hys} of these compounds can also be reduced to 2 K in low Fe/Mn and P/Si ratio compounds without losing giant MCE [14,18]. The Curie temperature (T_c) of MnFe(P,Si) compounds can be adjusted in the vicinity of room temperature by changing the Fe/Mn or P/Si ratio [14,18,19]. The discovery of MnFe(P,Si) magnetic refrigerants materials with high-performance and relatively low-cost paves the effective way for commercialization of magnetic refrigeration and magnetocaloric power-conversion. However, systematic study of the Si- and Mn-rich MnFe(P,Si) alloys has not been addressed in former reports.

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In the present paper, we report the microstructure, magnetic phase transition, isothermal magnetic-entropy change and direct measurement of an adiabatic temperature change close to room temperature for Si- and Mn-rich $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ ($x = 1.25, 1.30, 1.35, 1.40, 1.45$ and 1.50) alloys.

EXPERIMENTAL DETAILS

$\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ ($x = 1.25, 1.30, 1.35, 1.40, 1.45$ and 1.50) alloys were synthesized by a high energy ball milling and solid state reaction method. The starting materials, Mn (purity 99.9 %), Si (purity 99.999 %), red P (purity 99.999 %) and Fe powder (purity 99.8 %), were milled under N_2 atmosphere in a high energy ball mill for 3 h. After milling, the powder was pressed into pellets under a pressure of 3.9×10^8 Pa and sealed in quartz ampoules under Ar atmosphere. Then, the ampoules were heated at 1100°C for 2 h and then homogenized at 850°C for 20 h. Finally, they were slowly cooled down to room temperature. Powder X-ray diffraction (XRD) experiments of the samples were performed at room temperature by using a Philips PW1830 diffractometer with Cu K α radiation. A Hitachi S3400N scanning electron microscope (SEM) was used to investigate the microstructure of the samples. The energy-dispersive X-ray spectrometry (EDX) was used to detect the compositions of the samples. Magnetization measurements were carried out by using a Lakeshore 7407 type vibrating sample magnetometer (VSM). The direct measurement of the adiabatic temperature change was carried out in a homemade magnetocaloric effect measuring device under a magnetic field of 1.48 T. In this apparatus, sintered Nd-Fe-B permanent magnets were assembled to generate a static magnetic-field, which worked as the magnetic field source in the measurement [13]. Experimental errors for the direct measurement technique were estimated to be ± 0.1 K [20,21].

Isothermal magnetic-entropy change can be derived by using the Maxwell relation [22]

$$\Delta S_m(T, B) = \int_0^B \left(\frac{\partial M}{\partial T} \right)_B dB. \quad (1)$$

For magnetization measurements performed at discrete temperature, ΔS_m can be calculated numerically by

$$\Delta S_m(T, \Delta B) = \sum_i \frac{M_i(T + \Delta T/2, B_i) - M_i(T - \Delta T/2, B_i)}{\Delta T} \Delta B_i, \quad (2)$$

where $M_i(T + \Delta T/2, B_i)$ and $M_i(T - \Delta T/2, B_i)$ represent the values of the magnetization in a magnetic field B_i at the temperatures $T + \Delta T/2$ and $T - \Delta T/2$, respectively, and ΔB is the magnetic field change.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ ($x = 1.25, 1.30, 1.35, 1.40, 1.45$ and 1.50) alloys. The results indicate that only $\text{Fe}_{0.65}\text{Mn}_{1.25}\text{P}_{0.4}\text{Si}_{0.6}$ alloy crystallizes into a single Fe_2P -type hexagonal structure, and other samples contain a small amount of mixture phases with $(\text{Fe,Mn})_3\text{Si}$ and $(\text{Fe,Mn})_5\text{Si}_3$. The variation of the lattice parameters a , c and c/a with increasing Mn substitution for Fe_2P -type structure are listed in Table 1. The SEM backscattered electron

Figure 1 XRD patterns of the $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ ($x = 1.25, 1.30, 1.35, 1.40, 1.45$ and 1.50) alloys at room temperature.

Table 1 Curie temperature (T_c), thermal hysteresis (T_{hys}), maximum isothermal magnetic entropy change ($-\Delta S_{\text{max}}$) and maximum adiabatic temperature change ($\Delta T_{\text{ad}}^{\text{max}}$) of $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys

Compositions	x	a (Å)	c (Å)	c/a	T_c (K)	ΔT_{hys} (K)	$-\Delta S_{\text{max}}$ (J (kg K) $^{-1}$) ($\Delta B = 1.5$ T)	$\Delta T_{\text{ad}}^{\text{max}}$ (K) ($\Delta B = 1.48$ T)
$\text{Fe}_{0.75}\text{Mn}_{1.25}\text{P}_{0.4}\text{Si}_{0.6}$	1.25	6.194	3.338	0.539	321	4	7.2	—
$\text{Fe}_{0.70}\text{Mn}_{1.30}\text{P}_{0.4}\text{Si}_{0.6}$	1.30	6.175	3.363	0.545	313	4	5.5	1.8
$\text{Fe}_{0.65}\text{Mn}_{1.35}\text{P}_{0.4}\text{Si}_{0.6}$	1.35	6.139	3.418	0.557	298	1	5.6	1.8
$\text{Fe}_{0.60}\text{Mn}_{1.40}\text{P}_{0.4}\text{Si}_{0.6}$	1.40	6.141	3.411	0.555	286	2	3.6	1.5
$\text{Fe}_{0.55}\text{Mn}_{1.45}\text{P}_{0.4}\text{Si}_{0.6}$	1.45	6.146	3.417	0.556	275	3	3.0	1.1
$\text{Fe}_{0.50}\text{Mn}_{1.50}\text{P}_{0.4}\text{Si}_{0.6}$	1.50	6.147	3.417	0.556	266	2	2.6	—

images of $\text{Fe}_{0.75}\text{Mn}_{1.25}\text{P}_{0.4}\text{Si}_{0.6}$ and $\text{Fe}_{0.5}\text{Mn}_{1.5}\text{P}_{0.4}\text{Si}_{0.6}$ samples show that two miscellaneous phases (corresponding to the black and white area, respectively) and large number of holes distribute in the matrix, as shown in Fig. 2. The EDX analysis identifies that the compositions of white and black phase are $(\text{Fe,Mn})_{72}\text{Si}_{28}$ and $(\text{Fe,Mn})_{63}\text{Si}_{37}$, respectively, which is consistent with the XRD result. $\text{Fe}_{0.5}\text{Mn}_{1.5}\text{P}_{0.4}\text{Si}_{0.6}$ alloy contains more $(\text{Fe,Mn})_3\text{Si}$ phase than $\text{Fe}_{0.75}\text{Mn}_{1.25}\text{P}_{0.4}\text{Si}_{0.6}$ alloy. It means that excessive Mn content is not conducive to the formation of Fe_2P -type structure. The precipitation of $(\text{Fe,Mn})_3\text{Si}_3$ phase is closely related to the Fe/Mn ratio in $\text{MnFe}(\text{P,Si})$ alloys, as it is not observed in higher Fe/Mn ratio alloys [23–25]. This phenomenon can also be verified in $\text{MnFe}(\text{P,Ge})$ alloys [26].

Fig. 3a presents the temperature dependence of the magnetization (M - T) for the $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ ($x = 1.25, 1.30, 1.35, 1.40, 1.45$ and 1.50) alloys measured during cooling and heating under a magnetic field of 0.05 T. The T_c of alloys is defined as the extreme of the derivative dM/dT versus T curves in heating process as shown in Fig. 3b. The value of T_c decreases linearly with the increasing content of Mn,

Figure 3 Temperature dependences of M (a) and dM/dT for $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys in applied field of 0.05 T (b).

Figure 2 SEM backscattered electron images of $\text{Fe}_{0.75}\text{Mn}_{1.25}\text{P}_{0.4}\text{Si}_{0.6}$ (a) and $\text{Fe}_{0.5}\text{Mn}_{1.5}\text{P}_{0.4}\text{Si}_{0.6}$ alloys (b).

Figure 4 Dependence of Curie temperature on the Mn content of $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys.

as shown in Fig. 4 and Table 1. This tendency is in good agreement with the previous investigation of $\text{Mn}_{2-y}\text{Fe}_y\text{P}_{0.75}\text{Ge}_{0.25}$ compounds [10]. In $\text{MnFe}(\text{P,Si})$ compounds, Fe, Mn, P and Si atoms enter preferentially the 3f, 3g, 1b and 2c sites, respectively, and the exchange coupling interaction of nearest Mn-Fe is much stronger than that of Fe-Fe and Mn-Mn atomic pairs [27]. The excess Mn atoms have to occupy the 3f sites in high Mn/Fe ratio compounds [14]. Therefore, the increases of Mn atoms in $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys lead to a decrease of Mn-Fe atomic pair, which weakens the ferromagnetic exchange interaction of alloys. This is the main reason for the linear decr-

Figure 5 Isothermal magnetizations of the furnace-cooled $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys with x values of 1.25 (a), 1.30 (b), 1.35 (c), 1.40 (d), 1.45 (e) and 1.50 (f).

ease of T_c in the $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys with increasing Mn content. A more detailed analysis of the lattice parameters confirms that the c/a ratio increases with increasing the Mn/Fe ratio in alloys without minor impurity phase, which also results in a decrease in T_c [13]. However, c/a ratio does not increase continuously with the increasing Mn content in our experimental results, which indicates that this rule is not suitable for the alloys containing impurity phase. This result can also be observed in the $\text{Mn}_{1.35}\text{Fe}_{0.65}\text{P}_{1-x}\text{Si}_x$ alloys [18]. The heating or cooling dM/dT curves of samples con-

tain only a single symmetric ferromagnetic-paramagnetic phase transition peak (Fig. 3b), and magnetization tends to 0 at high temperature in M - T curves, which indicates that the impurity phases of $(\text{Fe,Mn})_3\text{Si}$ and $(\text{Fe,Mn})_5\text{Si}_3$ exhibit a paramagnetic nature in our experimental temperature range. The ΔT_{hys} values of the $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ ($x = 1.25, 1.30, 1.35, 1.40, 1.45$ and 1.50) alloys are 4, 4, 1, 2, 3 and 2 K, respectively, as listed in Table 1. ΔT_{hys} can be reduced effectively by decreasing the Fe/Mn ratio. In particular, the ΔT_{hys} value of $\text{Fe}_{0.65}\text{Mn}_{1.35}\text{P}_{0.4}\text{Si}_{0.6}$ alloy can only

reach 1 K, which is mainly attributed to the shortage of impurity phase in this alloy. Nevertheless, all the alloys exhibit very low ΔT_{hys} , which is beneficial for avoiding efficiency decrease of magnetic refrigeration.

Arrott plot method is an effective way to obtain the information of the phase transition. From the measured data of increasing field isothermal magnetizations (Fig. 5), the Arrott plots of the $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys are obtained and shown in Fig. 6. The Arrott plot of $\text{Fe}_{0.75}\text{Mn}_{1.25}\text{P}_{0.4}\text{Si}_{0.6}$ alloy shows a tiny negative slope which confirms the occurrence of a weakened FOMT. However, neither a negative slope nor an inflection point can be observed when Mn content is higher than 1.25, indicating a second-order magnetic transition (SOMT) behavior. The SOMT becomes obviously with increasing Mn content. This result is in agreement with previous study [13].

Based on the isothermal magnetizations data, the $-\Delta S_{\text{m}}$ of $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys can be quantified by Maxwell equation. Fig. 7a displays the temperature dependence of the $-\Delta S_{\text{m}}$ for $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys under a magnetic field change of 0–1.5 T. The $-\Delta S_{\text{max}}$ values of $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ ($x = 1.25, 1.30, 1.35, 1.40, 1.45$ and 1.50) are about 7.2, 5.5, 5.6, 3.6, 3.0 and 2.6 $\text{J} (\text{kg K})^{-1}$, respectively. The $-\Delta S_{\text{max}}$ values of most $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys are larger than that of Gd (about 3.3 $\text{J} (\text{kg K})^{-1}$ in a magnetic field change of 0–1.5 T). The $-\Delta S_{\text{max}}$ of $\text{Fe}_{0.65}\text{Mn}_{1.35}\text{P}_{0.4}\text{Si}_{0.6}$ alloy is larger than that of the other alloys with similar compositions, which means that the single phase alloy has a relatively high MCE. Fig. 7b displays the temperature dependence of the ΔT_{ad} for the $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys within a field change of 0–1.48 T. The $\Delta T_{\text{ad}}^{\text{max}}$ values of $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ ($x = 1.30, 1.35, 1.40$ and 1.45) alloys are about 1.8, 1.8, 1.5 and 1.1 K, respectively. All $\Delta T_{\text{ad}}^{\text{max}}$ values are larger than that of $\text{Ni}_{50.2}\text{Mn}_{39.8}\text{In}_{10}$ and $\text{LaFe}_{11}\text{Co}_{0.9}\text{Si}_{1.1}$ compounds in the same

Figure 6 Arrott plots of $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ ($x = 1.25, 1.30, 1.35, 1.40, 1.45$ and 1.50) alloys obtained from the increasing field isothermal magnetizations measured in the vicinity of their critical temperatures.

Figure 7 Isothermal magnetic-entropy changes ($-\Delta S_{\text{m}}$) (a) and adiabatic temperature changes (ΔT_{ad}) of $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys (b).

magnetic field change [28,29]. The $-\Delta S_{\text{max}}$ and $\Delta T_{\text{ad}}^{\text{max}}$ values are listed in Table 1. In summary, small ΔT_{hys} with giant MCE can be achieved in $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ ($x = 1.25, 1.30, 1.35, 1.40, 1.45$ and 1.50) alloys.

CONCLUSIONS

$\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ serial alloys crystallize into a majority Fe_2P -type structure, coexisting with minor amounts of $(\text{Mn},\text{Fe})_5\text{Si}$ and $(\text{Mn},\text{Fe})_5\text{Si}_3$ phases. The direct measurement of an adiabatic temperature change close to room temperature for $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys is achieved. The maximum adiabatic temperature change of $\text{Fe}_{0.7}\text{Mn}_{1.3}\text{P}_{0.4}\text{Si}_{0.6}$ and $\text{Fe}_{0.65}\text{Mn}_{1.35}\text{P}_{0.4}\text{Si}_{0.6}$ alloys can reach up to 1.8 K under a magnetic field change of 0–1.48 T. The maximum isothermal magnetic-entropy change of the alloys decreases from 7.2 to 2.6 $\text{J} (\text{kg K})^{-1}$ with increasing Mn-content from 1.25 to 1.5 under a magnetic field variation of 0–1.5 T. The single phase alloy shows a low thermal hysteresis and a relatively high MCE in all alloys. The suitable magnetocaloric effects, low thermal hysteresis and low materials cost of Si- and Mn-rich $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ alloys make them a promising candidate material for room temperature magnetic refrigeration applications.

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- Brück E, Tegus O, Thanh DTC, *et al.* Magnetocaloric refrigeration near room temperature. *J Magn Magn Mater*, 2007, 310:

- 2793–2799
- 2 Gschneidner Jr KA, Pecharsky VK, Tsokol AO. Recent developments in magnetocaloric materials. *Rep Prog Phys*, 2005, 68: 1479–1539
 - 3 Brück E. Developments in magnetocaloric refrigeration. *J Phys D-Appl Phys*, 2005, 38: R381–R391
 - 4 Tegus O, Brück E, Zhang L, *et al.* Magnetic-phase transitions and magnetocaloric effects. *Phys B-Cond Matter*, 2002, 319: 174–192
 - 5 Bednarz G, Geldart DJW, White MA. Heat capacity of gadolinium near the Curie temperature. *Phys Rev B*, 1993, 47: 14247–14259
 - 6 Pecharsky VK, Gschneidner, Jr. KA. Giant magnetocaloric effect in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$. *Phys Rev Lett*, 1997, 78: 4494–4497
 - 7 Hu F, Shen B, Sun J, *et al.* Influence of negative lattice expansion and metamagnetic transition on magnetic entropy change in the compound $\text{LaFe}_{11.4}\text{Si}_{1.6}$. *Appl Phys Lett*, 2001, 78: 3675
 - 8 Wada H, Tanabe Y. Giant magnetocaloric effect of $\text{MnAs}_{1-x}\text{Sb}_x$. *Appl Phys Lett*, 2001, 79: 3302
 - 9 Tegus O, Brück E, Buschow KHJ, *et al.* Transition-metal-based magnetic refrigerants for room-temperature applications. *Nature*, 2002, 415: 150–152
 - 10 Trung NT, Zhang L, Caron L, *et al.* Giant magnetocaloric effects by tailoring the phase transitions. *Appl Phys Lett*, 2010, 96: 172504
 - 11 Tegus O, Fuquan B, Dagula W, *et al.* Magnetic-entropy change in $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.7}\text{As}_{0.3-x}\text{Ge}_x$. *J Alloys Compd*, 2005, 396: 6–9
 - 12 Dagula W, Tegus O, Li XW, *et al.* Magnetic properties and magnetic-entropy change of $\text{MnFeP}_{0.5}\text{As}_{0.5-x}\text{Si}_x$ ($x = 0\text{--}0.3$) compounds. *J Appl Phys*, 2006, 99: 08Q105
 - 13 Trung NT, Ou ZQ, Gortenmulder TJ, *et al.* Tunable thermal hysteresis in MnFe(P,Ge) compounds. *Appl Phys Lett*, 2009, 94: 102513
 - 14 Dung NH, Ou ZQ, Caron L, *et al.* Mixed magnetism for refrigeration and energy conversion. *Adv Energy Mater*, 2011, 1: 1215–1219
 - 15 Yibole H, Guillou F, Zhang L, *et al.* Direct measurement of the magnetocaloric effect in MnFe(P, X) ($X = \text{As, Ge, Si}$) materials. *J Phys D-Appl Phys*, 2014, 47: 075002
 - 16 Tegus O, Bao LH, Song L. Phase transitions and magnetocaloric effects in intermetallic compounds MnFeX ($X = \text{P, As, Si, Ge}$). *Chin Phys B*, 2013, 22: 037506
 - 17 Huliageqi B, Geng Y, Li Y, *et al.* A significant reduction of hysteresis in MnFe(P,Si) compounds. *J Korean Phys Soc*, 2013, 63: 525–528
 - 18 Geng YX, Tegus O, Bi LG. Magnetocaloric effects in $\text{Mn}_{1.35}\text{Fe}_{0.65}\text{P}_{1-x}\text{Si}_x$ compounds. *Chin Phys B*, 2012, 21: 037504
 - 19 Geng YX, Tegus O, Blige Q, *et al.* Magnetocaloric properties of $\text{Mn}_{2-x}\text{Fe}_x\text{P}_{0.51}\text{Si}_{0.49}$. In: Proceedings of the Fourth International Conference on Magnetic Refrigeration at Room Temperature. Baotou, 2011, 213–217
 - 20 Zeng H, Zhang J, Kuang C, *et al.* Direct measurements of magnetocaloric effect of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ alloys in low magnetic field. *J Supercond Nov Magn*, 2012, 25: 487–490
 - 21 Huang JH, Qiu JF, Liu JR, *et al.* A direct measurement setup for magnetocaloric effect. In: Proceedings of the First International Conference on Magnetic Refrigeration at Room Temperature. Montreux, 2005, 179–181
 - 22 Hashimoto T, Numasawa T, Shino M, *et al.* Magnetic refrigeration in the temperature range from 10 K to room temperature: the ferromagnetic refrigerants. *Cryogenics*, 1981, 21: 647–653
 - 23 Geng YX, Tegus O. Experimental study on the magnetocaloric effect in $\text{Mn}_{1.2}\text{Fe}_{0.8-x}\text{Co}_x\text{P}_{0.48}\text{Si}_{0.52}$ compounds. *J Magn Mater Dev*, 2011, 42: 17–20
 - 24 Geng YX, Tegus O, Bi LG, *et al.* Influence of different preparation techniques and raw materials on magnetocaloric effect in $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{0.48}\text{Si}_{0.52}$ compound. *J Chin Rare Earth Soc*, 2011, 29: 266–270
 - 25 Zheng ZG, Tan ZC, Yu HY, *et al.* Structural, magnetic properties and magnetocaloric effect of $\text{Mn}_{1.2}\text{Fe}_{0.8}\text{P}_{1-x}\text{Si}_x\text{B}_{0.03}$ compounds. *Mater Res Bull*, 2016, 77: 29–34
 - 26 Yan A, Müller KH, Schultz L, *et al.* Magnetic entropy change in melt-spun MnFePGe . *J Appl Phys*, 2006, 99: 08K903
 - 27 Liu XB, Altounian Z. A first-principles study on the magnetocaloric compound $\text{MnFeP}_{2/3}\text{Si}_{1/3}$. *J Appl Phys*, 2009, 105: 07A902–07A902
 - 28 Buchelnikov V, Taskaev S, Drobosyuk M, *et al.* Magnetocaloric effect in Ni-Mn-X ($X = \text{Ga, In}$) Häusler alloys. In: Proceedings of the Fourth International Conference on Magnetic Refrigeration at Room Temperature. Baotou, 2010, 31–36
 - 29 Balli M, Fruchart D, Sari O, *et al.* Direct measurement of the magnetocaloric effect on $\text{La}(\text{Fe}_{13-x-y}\text{Co}_y)\text{Si}_x$ compounds near room temperature. *J Appl Phys*, 2009, 106: 023902

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Conflict of interest The authors declare that they have no conflict of interest.

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$\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ 合金的显微组织、磁性和磁热效应

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摘要 本文系统研究了富Si, Mn的FeMn(P,Si)合金的显微组织、磁性和磁热效应. 利用高能球磨和固态烧结法制备了 $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ ($x = 1.25, 1.30, 1.35, 1.40, 1.45$ 和 1.50)系列合金. 实验结果表明, 合金主要形成了 Fe_2P 型六角结构相, 伴有少量 $(\text{Mn,Fe})_3\text{Si}$ 和 $(\text{Mn,Fe})_5\text{Si}_3$ 相的析出. 合金的Curie温度(T_c)随着Mn含量的增加而逐渐降低, 由 $x=1.25$ 时的321 K降低到 $x=1.5$ 时的266 K. 随着Mn含量的增加, 合金逐渐由一级磁相变过程向二级磁相变过程转变. $\text{Fe}_{0.75}\text{Mn}_{1.25}\text{P}_{0.4}\text{Si}_{0.6}$ 合金具有最大等温磁熵变($-\Delta S_{\text{max}}$), 在0–1.5 T磁场变化下的 $-\Delta S_{\text{max}}$ 为 $7.2 \text{ J (kg K)}^{-1}$. $\text{Fe}_{0.7}\text{Mn}_{1.3}\text{P}_{0.4}\text{Si}_{0.6}$ 和 $\text{Fe}_{0.65}\text{Mn}_{1.35}\text{P}_{0.4}\text{Si}_{0.6}$ 合金在0–1.48 T磁场变化下的最大绝热温变(ΔT_{ad})为1.8 K. 所有合金的热滞都低于4 K. $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{0.4}\text{Si}_{0.6}$ 系列合金可作为室温磁制冷的理想候选材料.