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Magnetocaloric effect in $LaFe_{11.8-x}Co_xSi_{1.2}$ melt-spun ribbons

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Abstract

The structure and magnetic entropy changes in melt-spun and annealed $LaFe_{11.8-x}Co_xSi_{1.2}$ ($x = 0$, 0.4 and 0.8) ribbons have been investigated. It is found that the value of T_c can be increased continuously up to 290 K for $x = 0.8$ and the phase transition, at T_c from paramagnetic to ferromagnetic, is changed from first- to second-order due to Co substitution. Large values of the magnetic entropy change are 31 and 13.5 J/kg K in the magnetic field change from 0 to 5 T at 201 K for the $LaFe_{11.8}Si_{1.2}$ and at 290 K for the $LaFe_{11}Co_{0.8}Si_{1.2}$ ribbons, respectively. The magnetic entropy change in the $LaFe_{11}Co_{0.8}Si_{1.2}$ ribbons is higher than that reported in the bulk counterpart and that of conventional MCE materials, such as pure Gd. The enhanced magnetic entropy change of ribbons compared to bulk counterpart is attributed to a more uniform microstructure and element distribution resulting from the high cooling rate by melt-spinning.

Keywords: Magnetocaloric effect; Magnetic entropy change; $LaFe_{11.8-x}Co_xSi_{1.2}$; Phase transition

1. Introduction

Magnetic refrigeration based on the magnetocaloric effect (MCE) has attracted much attention because of its numerous potential advantages over vapour-compression refrigeration. The search for a room temperature magnetic refrigerant is of special interest [1–3]. Conventional MCE materials, pure Gd, has the highest MCE involving a second-order magnetic transition, which shows maximum entropy change, ΔS, of 9.7 J/kg K under a 5 T magnetic field at $T_c = 293$ K [4]. However, the high price of Gd and moderate value of magnetic entropy change limit its wide application. $LaFe_{13-x}Si_x$ compounds with $NaZn_{13}$-type structure are promising materials for magnetic refrigeration due to their excellent soft ferromagnetism, high magnetization and low cost [5–9]. The thermal conductivity, an important characteristic for magnetic refrigerants, of the $LaFe_{13-x}Si_x$, is comparable with that of Gd and much higher than those of $Gd_5(Si,Ge)_4$ and MnAs [10]. However, a prolonged heat treatment (~1 month, 1000 °C) is necessary to develop the $NaZn_{13}$-type phase in the bulk alloys [5–9].

Recently, melt-spinning was used to produce $La(Fe_{1-x}Si_x)_{13}$ materials [11] and the 1:13 phase could be developed by a much shortened annealing [12,13]. The Curie temperature is increased and the magnetic and thermal hysteresis are decreased in the melt-spun-type $LaFe_{11.57}Si_{1.43}$ materials, compared with those in conventional bulk alloys. From the practical viewpoint, it is important to control the temperature range of the large MCE. The substitution of Co for Fe results in an increase of T_c [8]. In this work, we report on structure and magnetic entropy changes in melt-spun and annealed $LaFe_{11.8-x}Co_xSi_{1.2}$ ($x = 0$, 0.4 and 0.8) ribbons. A large value of magnetic entropy change is obtained at room temperature in Co-substituted ribbons.

2. Experimental

$LaFe_{11.8-x}Co_xSi_{1.2}$ alloys were prepared by arc melting in an Ar gas atmosphere. Pieces of ingots were then inserted into a quartz tube with a nozzle. The chamber was evacuated to a vacuum of 10^{-2} Pa and then filled with high purity Ar. The samples were induction melted and ejected through the nozzle using a pressure difference. The surface speed of the Cu wheel was 40 m/s. The as-spun ribbons were subsequently annealed at 1050 °C for 1 h and then quenched to room temperature. The structure of samples was characterized using X-ray powder diffraction with Co Kα radiation. Magnetic measurements were carried out using a 5 T-SQUID magnetometer (Quantum Design). The temperature increment is 3 K and the sweep rate of magnetic field is slow enough to ensure *M–H* curves in an isothermal process.

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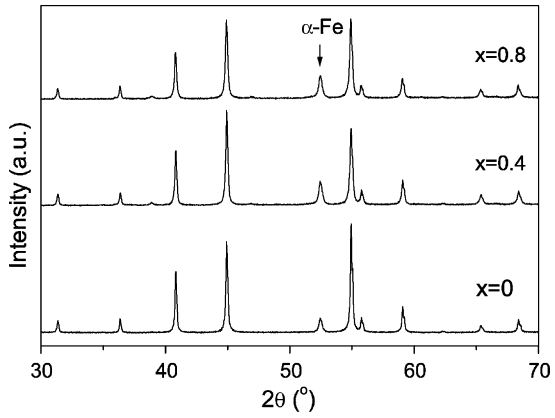

Fig. 1. XRD patterns of $LaFe_{11.8-x}Co_xSi_{1.2}$ ribbons.

Table 1
The lattice constant a, Curie temperature T_c and magnetic entropy change of $LaFe_{11.8-x}Co_xSi_{1.2}$ ribbons

x	Lattice constant a (Å)	T_c (K)	ΔS (J/kg K) (5 T)
0	11.46	195	31
0.4	11.47	247	17.4
0.8	11.49	290	13.5

3. Results and discussions

XRD patterns (Fig. 1) show that the main phase in all three ribbons is cubic $NaZn_{13}$-type phase, additionally a small amount of α-Fe is detected (indicated by an arrow). No obvious shift of XRD patterns was observed due to Co substitution, indicating that the lattice parameters remain largely unchanged. Similar results were found for bulk $La(Fe,Co,Si)_{13}$ [14] and $La(Fe,Co,Al)_{13}$ [15] compounds (Table 1).

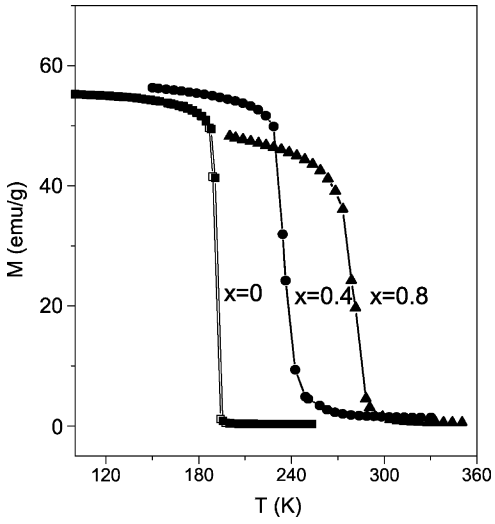

Fig. 2. Temperature dependence of the magnetization of $LaFe_{11.8-x}Co_xSi_{1.2}$ ($x = 0$, 0.4 and 0.8) ribbons under a magnetic field of 100 Oe.

The temperature dependence of magnetization are shown in Fig. 2. T_c increases nearly linearly with Co content and can be easily controlled between 200 and 290 K, which is useful for magnetic refrigerant operating near room temperature. The significant improvement of T_c is attributed to the strong Co–Fe exchange interaction [14]. In addition, a very sharp change of magnetization takes place at 195 K for $x = 0$ and a clear temperature hysteresis upon heating and cooling was observed, indicating a first-order magnetic phase transition. With increasing Co, the magnetization gradually decreases with increasing temperature near T_c, which would imply a reduction of magnetic entropy change. However, the samples exhibit a completely reversible behavior near T_c upon heating and cooling, indicating a second-order phase transition and the reversible behavior of

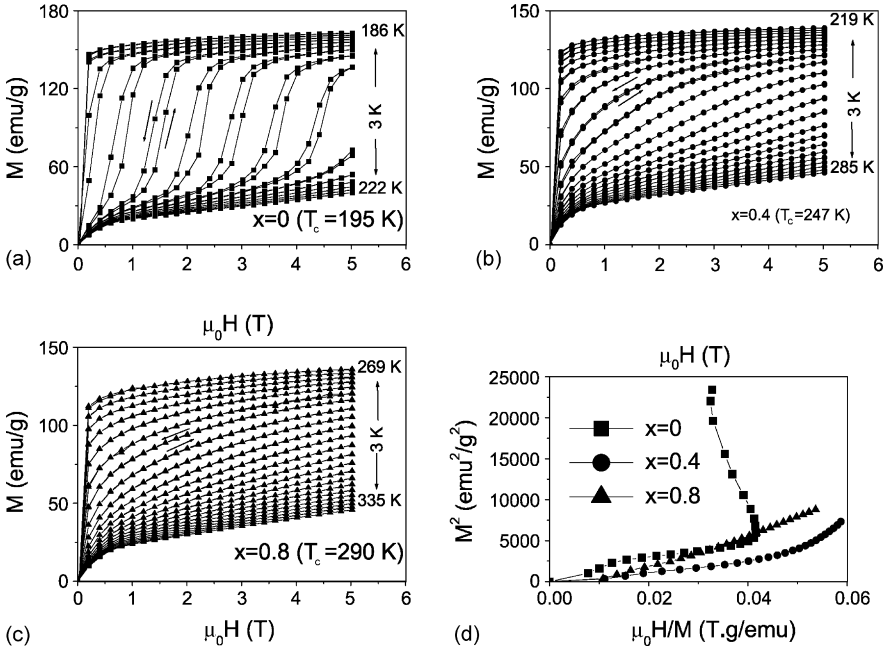

Fig. 3. The isothermal magnetization and Arrott plots just above the respective Curie temperatures of $LaFe_{11.8-x}Co_xSi_{1.2}$ ribbons.

magnetic entropy change in a temperature cycle for the ribbons with $x = 0.4$ and 0.8.

Measurements of magnetization isotherms of the ribbons as a function of applied magnetic field up to 5 T at different temperatures in a wide temperature range near T_c are shown in Fig. 3. With increasing the measurement temperature above T_c, the $LaFe_{11.8-x}Co_xSi_{1.2}$ ribbons with $x = 0$ show a sharp change of the magnetization with clear magnetic hysteresis above a critical field H_c. The critical fields increase with temperature, which is typical for a field-induced first-order magnetic phase transition from the paramagnetic to the ferromagnetic state, comparable to that observed in the bulk $La(Fe_{1-x}Si_x)_{13}$ alloys with low Si concentration [9]. Thus, the discontinuous volume change and the coexistence of both ferromagnetic and paramagnetic states due to supercooling phenomenon near T_c in bulk alloy [16] should also be expected in the melt-spun materials, which will be investigated later. When Co is introduced, the sharp jump of the magnetization and magnetic hysteresis almost disappear, indicating that the phase transition, at T_c from paramagnetic to ferromagnetic, is changed from first- to second-order, in agreement with M–T measurements shown in Fig. 2. The very small magnetic hysteresis upon a field cycle reveals a good reversibility of magnetic entropy change on the applied field. The observed nonlinear field dependence of magnetization above T_c, is attributed to the α-Fe phase, consistent with the X-ray diffraction analysis. Arrott plots [17] show the negative slopes for the $LaFe_{11.8}Si_{1.2}$ ribbons and an almost monotonic increase for $LaFe_{11.4}Co_{0.4}Si_{1.2}$ and $LaFe_{11}Co_{0.8}Si_{1.2}$ ribbons (Fig. 3(d)), further confirming the occurrence of a first-order transition in the Co-free ribbon and a second-order magnetic transition in the Co-substituted ribbons.

The magnetic entropy change ΔS can be calculated using the Maxwell relation and the collected magnetization data [18]. This indirect method has been believed to be a reliable way to evaluate magnetic materials of magnetic refrigeration. Fig. 4 displays the magnetic entropy changes of the $LaFe_{11.8-x}Co_xSi_{1.2}$ samples upon field increase as a function of temperature. A large value of maximum $|\Delta S| = 31$ J/kg K, resulting from the rapid change of magnetization at the T_c, was obtained in $LaFe_{11.8}Si_{1.2}$ ribbon at 201 K under 5 T. Co substitution leads to a reduction in the values of magnetic entropy changes, which is attributed to the different nature of the magnetic phase transition in the ribbons, as mentioned above. However, the temperatures corresponding to the maximum $|\Delta S|$ are shifted to higher temperature due to enhancement of T_c by Co. $LaFe_{11}Co_{0.8}Si_{1.2}$ ribbon shows a value of 13.5 J/kg K at 290 K under 5 T. This value is higher than that reported in bulk $La(Fe,Co,Si)_{13}$ alloy [14] and that of conventional MCE materials, such as pure Gd. The enhanced magnetic entropy change is attributed to a uniform microstructure and element distribution resulting from the high cooling rate by melt-spinning, similar to that of the melt-spun $LaFe_{11.57}Si_{1.43}$ ribbons observed by scanning electron microscopy and energy-dispersive spectroscopy [12]. Reduced magnetic fields lead to lower peak values of $|\Delta S|$ in both $LaFe_{11.8}Si_{1.2}$ and $LaFe_{11}Co_{0.8}Si_{1.2}$ ribbons, as shown in Fig. 4(b) and (c). The value of $|\Delta S|$ of the $LaFe_{11}Co_{0.8}Si_{1.2}$ ribbons drops much faster with decreasing magnetic field change.

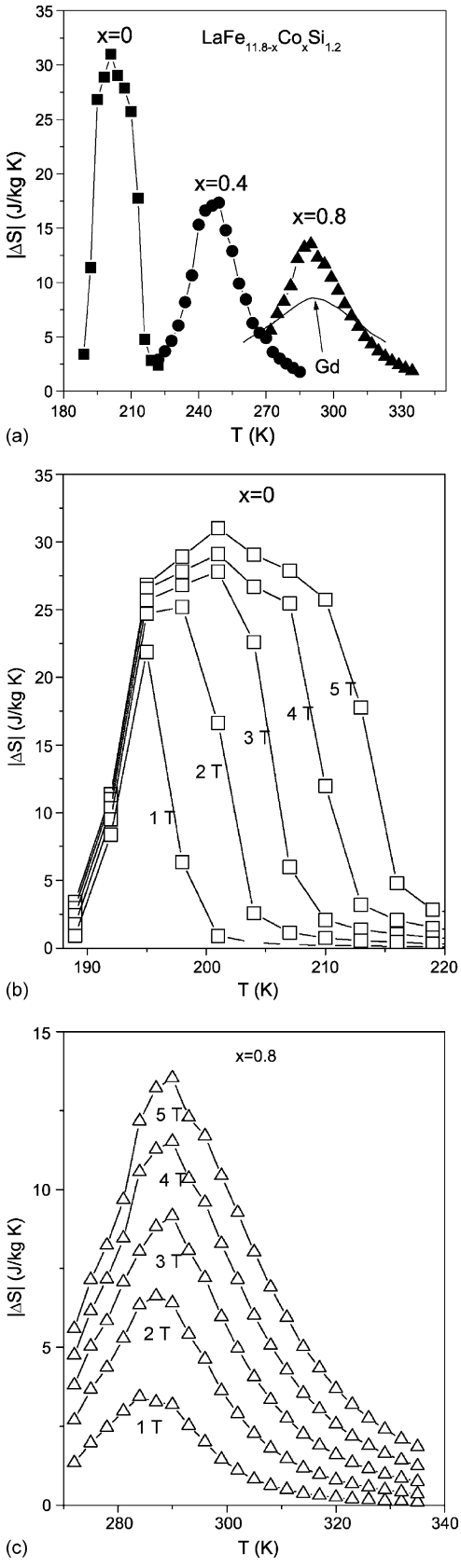

Fig. 4. Temperature dependence of the magnetic entropy change $|\Delta S|$ of (a) $LaFe_{11.8-x}Co_xSi_{1.2}$ ribbons under a magnetic field change of 0–5 T, (b) $x = 0$ and (c) $x = 0.8$ ribbons for the magnetic field changes of 0–1, 0–2, 0–3, 0–4 and 0–5 T [(a) contains Gd for comparison].

However, the very small hysteretic losses with relatively high value of magnetic entropy change in the $LaFe_{11}Co_{0.8}Si_{1.2}$ ribbons, related to second-order magnetic phase transition, could still lead to an improved cooling capacity, as discussed in Ref. [19]. Thus, the large magnetic entropy change, the significantly reduced magnetic and thermal hysteresis, and the much reduced processing time indicate that $La(Fe,Co,Si)_{13}$ ribbons are one of the most promising magnetic refrigerant materials, especially at room temperature.

4. Conclusions

The Curie temperature T_c of $La(Fe, Si)_{13}$ can be increased by Co substitution for Fe and the paramagnetic to ferromagnetic transition at T_c is changed from first- to second-order. Large values of the magnetic entropy change are obtained at room temperature in the $LaFe_{11}Co_{0.8}Si_{1.2}$ ribbons (13.5 J/kg K, 5 T at 290 K), which is higher than that of bulk bulk $La(Fe,Co,Si)_{13}$ alloy and that of pure Gd. The enhanced magnetic entropy change of the ribbons compared to bulk material is attributed to a more uniform microstructure and element distribution resulting from the high cooling rate by melt-spinning.

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