



Effects of solidification rate and excessive Fe on phase formation and magnetocaloric properties of $\text{LaFe}_{11.6x}\text{Si}_{1.4}$

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Abstract: The effects of solidification rate and excessive Fe on phase formation and magnetocaloric properties of $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ ($x=1.1, 1.2$) were investigated by XRD, SEM and VSM measurements. The XRD results show that the amount of LaFeSi phase in the as-cast melt-spun ribbons prepared by a copper wheel at a speed of 10 m/s is less than that in the as-cast arc melting buttons with the same x values. The annealed melt-spun ribbons contain smaller amount of $\text{La}(\text{Fe},\text{Si})_{13}$ (1:13) phase than the corresponding annealed arc melting buttons. Although the melt-spun sample has finer crystalline grains of α -Fe, as indicated by SEM analysis, its crystalline size has not reached nano-scale. Therefore, the magnetic exchange-coupling between 1:13 phase and α -Fe phase has not been observed in melt-spun ribbons. Further, the maximum negative magnetic entropy change ($-S_{\text{Max}}$) and relative cooling power (RCP) of annealed melt-spun ribbons under a field change of 0–2 T are weaker than those of the corresponding annealed arc melting buttons.

Key words: $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ alloy; solidification rate; microstructure; magnetocaloric properties

1 Introduction

Due to the coupling between field-induced paramagnetic (PM)–ferromagnetic (FM) transition and the discontinuous change of lattice constant, $\text{LaFe}_{13-x}\text{Si}_x$ alloys with cubic LaCo_{13} -type structure (hereinafter called 1:13 phase) exhibit some interesting physical properties, such as giant magnetocaloric effect (MCE). To maximize their MCE, researchers have tried their best to eliminate the impurities and obtain $\text{LaFe}_{13-x}\text{Si}_x$ with single 1:13 phase. However, due to the intrinsic characteristics of peritectic reaction $\text{Fe}+\text{LaFeSi}\rightarrow\text{La}(\text{Fe},\text{Si})_{13}$, α -Fe and LaFeSi phases co-exist proportionally in most annealed $\text{LaFe}_{13-x}\text{Si}_x$ samples [1–5]. It is well known that LaFeSi phase is corroded easily in some heat-conducting media [6,7], so its existence will deteriorate corrosion resistance of $\text{LaFe}_{13-x}\text{Si}_x$ alloys as magnetic refrigeration working materials. But α -Fe is a kind of soft magnetic materials and has remarkably high magnetic susceptibility; maybe a certain amount of α -Fe phase in $\text{LaFe}_{13-x}\text{Si}_x$ alloys can affect the magnetic behaviors of 1:13 phase, such as low field response

characteristics and MCE. In fact, the low field response effect has been reported in $\text{Gd}_5\text{Si}_2\text{Ge}_2/\text{Fe}$ composite magnetocaloric alloy [8]. Our previous work showed that excessive Fe in $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ buttons with $x>1$ prepared by arc melting results in reducing content of LaFeSi phase [9–11]. At the same time, the magnetocaloric properties of $\text{LaFe}_{11.6\times 1.1}\text{Si}_{1.4}$ are better than those of normal stoichiometric sample, which is an intriguing phenomenon. In addition, we found that the Curie temperatures (T_C) of 1:13 phase were all about 190 K in $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ alloys, and the magnetic coupling between 1:13 phase and α -Fe phase has not been observed. One possible reason is that the grain size of α -Fe phase is too large to generate strong exchange-coupling. If the grain size of α -Fe phase is decreased to a certain value, perhaps there exists a stronger exchange-coupling between magnetic atoms in 1:13 phase and α -Fe phase, which can affect T_C and magnetic properties.

Compared with arc melting $\text{LaFe}_{13-x}\text{Si}_x$ buttons, normal stoichiometric melt-spun $\text{LaFe}_{13-x}\text{Si}_x$ ribbons have lower content of 1:13 phases and MCE. The high solidification rate of melt-spun process results in small grain microstructure. For obtaining nonstoichiometric

LaFe_{11.6x}Si_{1.4} samples with different grain sizes of α -Fe phases, we used arc melting and melt-spun methods to prepare samples in this work. Up to now, the magnetic coupling between α -Fe phase and 1:13 phase in LaFe_{13-x}Si_x alloys has seldom been studied. It is very difficult to precisely explain the magnetic behavior of this complex multiphase system. Thus, we explored the effects of solidification rate and excessive α -Fe on phase formation and magnetic properties of nonstoichiometric LaFe_{11.6x}Si_{1.4} samples with $x=1.1$ and 1.2 only by comparing phase, microstructure and MCE.

2 Experimental

Approximately 15 g polycrystalline LaFe_{11.6x}Si_{1.4} buttons were prepared by using high-purity starting elements (99.4% La, 99.9% Fe, and 99.9999% Si, mass fraction). The components were arc-melted on a water-cooled copper hearth under high-purity argon atmosphere. The buttons were turned over and re-melted five times to achieve a homogeneous composition. Each button was cut into two parts on average. An half of each button was re-melted and then spun into ribbons by a single-roller melt-spinner with a copper wheel at a speed of 10 m/s under a purified argon atmosphere. As the temperature of 1523 K was close to up limit temperature of peritectic reaction, button and ribbon samples were annealed at 1523 K for 5 h in a molybdenum wire furnace with a vacuum of 3×10^{-3} Pa, followed by furnace cooling down to room temperature. The crystallographic structures were determined by powder X-ray diffraction (XRD) analysis using Cu K α radiation at room temperature. The microstructure and phase composition observations were carried out by scanning electron microscopy (SEM) and energy disperse spectroscopy (EDS) (Hitachi-S-3400N). Magnetic measurements were performed in vibrating-sample magnetometer (VSM, Lakeshore 7410) under a magnetic field up to 2 T.

3 Results and discussion

3.1 XRD analysis

Figure 1 displays the XRD patterns of the as-cast LaFe_{11.6x}Si_{1.4} samples with $x=1.1$ and 1.2 prepared by arc melting and melt-spinning, respectively. The main phase is α -Fe phase and the second phase is LaFeSi phase. The differences in solidification rates between melt-spun and arc melting processes affect phase relations and microstructure. The relative diffraction intensities of LaFeSi phase in the as-cast melt-spun LaFe_{11.6x}Si_{1.4} ribbons are weaker than those in arc melting LaFe_{11.6x}Si_{1.4} alloys with the same composition, which indicates that the content of LaFeSi phase is lower in ribbons. However, the diffraction peaks of 1:13 phase,

which appear in the as-cast arc melting buttons, almost cannot be observed in the as-cast melt-spun ribbons. This result is not consistent with the general points that the high solidification rates of melt-spun preparation enhance the formation of 1:13 phase and increase its content. According to our previous work [12], the temperatures of 1407.6 and 1530.5 K are melting point of LaFeSi phase and temperature of peritectic reaction, respectively. When annealing temperature is between 1407 and 1530 K, peritectic reaction will occur very fast, and the optimum annealing temperature will be about 1523 K [4]. The processing time is very short at 1407–1530 K in cooling process of melt-spun preparation; there is not enough time to complete the peritectic transformation. This behavior results in the fact that the content of 1:13 phase is lower in as-cast melt-spun LaFe_{11.6x}Si_{1.4} ribbons than in arc melting LaFe_{11.6x}Si_{1.4} buttons. In addition, the buttons need to be re-melted in melt-spun preparation, which leads to some loss of LaFeSi phase. Thus, the content of LaFeSi phase is lower in the as-cast LaFe_{11.6x}Si_{1.4} ribbons.

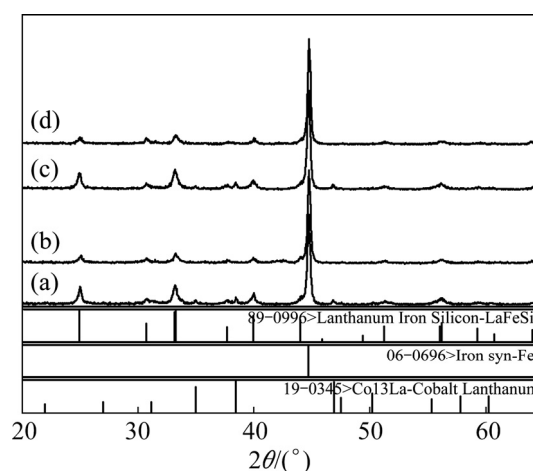


Fig. 1 XRD patterns of as-cast samples: (a) Arc melting LaFe_{11.6x1.1}Si_{1.4} button; (b) Melt-spun LaFe_{11.6x1.1}Si_{1.4} ribbon; (c) Arc melting LaFe_{11.6x1.2}Si_{1.4} button; (d) Melt-spun LaFe_{11.6x1.2}Si_{1.4} ribbon

Figure 2 shows the comparison of XRD patterns between arc melting and melt-spun LaFe_{11.6x}Si_{1.4} samples annealed at 1523 K for 5 h. The main phase is 1:13 phase and impurity phase is α -Fe phase. The relative diffraction intensities of α -Fe phase gradually increase with the increase of x . The diffraction peaks of LaFeSi phase almost disappear in the above two kinds of annealed LaFe_{11.6x}Si_{1.4} samples. By comparing with relative diffraction intensities of α -Fe phase, it can be found that the value in melt-spun LaFe_{11.6x}Si_{1.4} ribbons is higher than that in arc melting LaFe_{11.6x}Si_{1.4} alloys with the same x , which suggests that the annealed melt-spun ribbons contain larger amount of α -Fe phases. This can be

further confirmed by Rietveld refinement result, which shows that the mass fractions of α -Fe phase in arc melting samples with $x=1.1$ and 1.2 are 6.5% and 10.7%, but the corresponding values in melt-spun samples are 16.0% and 18.9%, respectively. This can be attributed to the lower content of LaFeSi phase in as-cast ribbons.

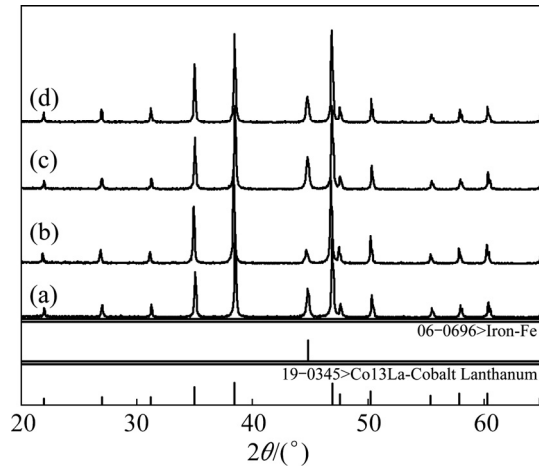


Fig. 2 XRD patterns of different samples annealed at 1523 K for 5 h: (a) Melt-spun $\text{LaFe}_{11.6 \times 1.1}\text{Si}_{1.4}$ ribbon; (b) Arc melting $\text{LaFe}_{11.6 \times 1.1}\text{Si}_{1.4}$ button; (c) Melt-spun $\text{LaFe}_{11.6 \times 1.2}\text{Si}_{1.4}$ ribbon; (d) Arc melting $\text{LaFe}_{11.6 \times 1.2}\text{Si}_{1.4}$ button

3.2 Microstructures and compositions

Figure 3 shows the back-scattered SEM images of the above two kinds of $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ samples. Grey matrix phase is 1:13 phase, black region is α -Fe phase and the white part is LaFeSi phase. The distribution of α -Fe phase is not homogeneous in all samples, but its grain size in melt-spun ribbons is much smaller than that in arc melting buttons. For example, the largest size in melt-spun $\text{LaFe}_{11.6 \times 1.1}\text{Si}_{1.4}$ is only about 3 μm , the corresponding size in arc melting sample is about 20 μm . Thus, the melt-spun technology is useful for grain refinement. Unfortunately, the melt-spun preparation in this work cannot refine the grain size of α -Fe phase to the nano-scale. The desired magnetic coupling between 1:13 phase and α -Fe phase will also be affected. In addition, it is hard to determine the amount of α -Fe phase from the limit number of SEM images due to its fine grain size and anisotropic distribution in matrix phase.

Since MCE is caused by 1:13 phase in $\text{LaFe}_{13-x}\text{Si}_x$ alloys, the element ratios in 1:13 phase should have a great influence on magnetic performance. Table 1 gives mole fractions of elements in 1:13 phases of two kinds of annealed $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ samples obtained by EDS analysis. It is clear that the mole fraction of Fe in those samples does not increase with the increase of x , indicating that

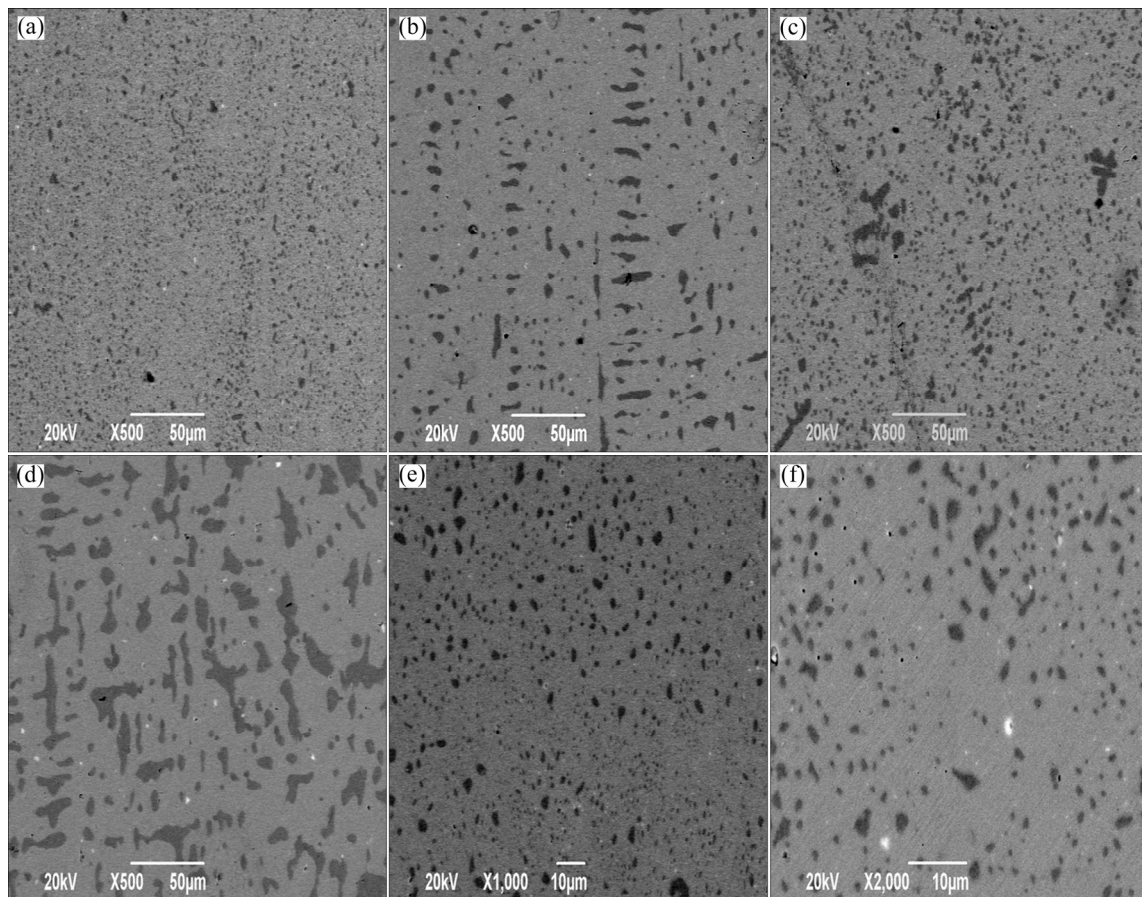


Fig. 3 SEM images: (a, e) Melt-spun $\text{LaFe}_{11.6 \times 1.1}\text{Si}_{1.4}$ ribbons; (b) Arc melting $\text{LaFe}_{11.6 \times 1.1}\text{Si}_{1.4}$ button; (c, f) Melt-spun $\text{LaFe}_{11.6 \times 1.2}\text{Si}_{1.4}$ ribbon; (d) Arc melting $\text{LaFe}_{11.6 \times 1.2}\text{Si}_{1.4}$ button

Table 1 Mole fractions of elements in 1:13 phases and magnetocaloric properties of $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ samples

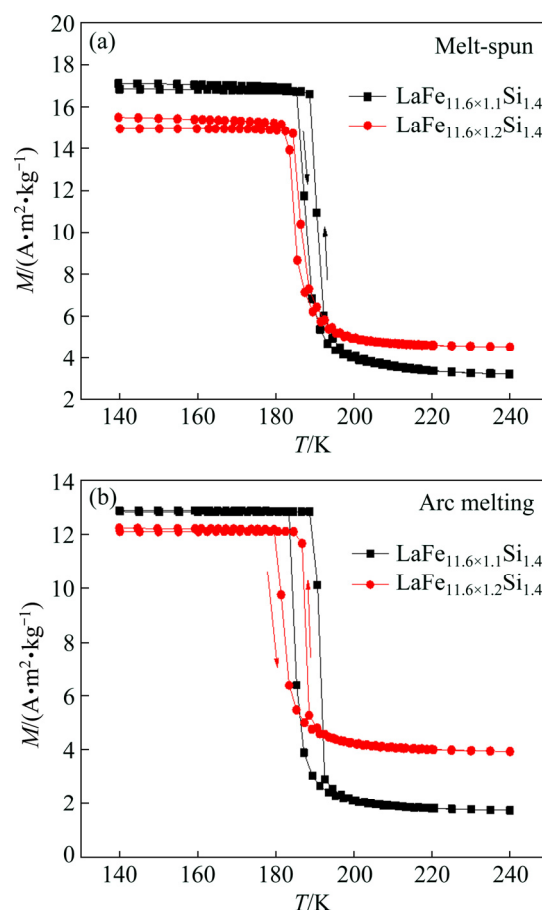
Preparation	x	Mole fraction/%			$T_{C\text{-ZFC}}/\text{K}$	$T_{C\text{-FC}}/\text{K}$	$-\Delta S_{\text{Max}}/(\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1})$	RCP/ $(\text{J}\cdot\text{kg}^{-1})$
		Fe	Si	La				
Melt-spun	1.1	80.09	12.79	7.11	190.5	187.3	17.2	146.2
Melt-spun	1.2	76.63	15.58	7.79	187.4	185.5	13.2	105.6
Arc melting	1.1	79.90	11.99	8.11	190.5	186.6	33.1	198.6
Arc melting	1.2	80.08	11.63	8.29	188.5	183.3	16.0	144.0

excessive Fe does not enter into 1:13 phase but exists as α -Fe phase. All element contents are very stable in two arc melting buttons. On the contrary, the contents are not stable in melt-spun $\text{LaFe}_{11.6\times 1.1}\text{Si}_{1.4}$ ribbons. This shows the existence of chemical component segregation in melt-spun samples. In total, La content in melt-spun $\text{LaFe}_{11.6\times 1.1}\text{Si}_{1.4}$ ribbons is smaller than that in arc melting $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ alloys, and Si content is just contrary. To the best of our knowledge, there are few reports about the effect of element content in 1:13 phase on magnetic properties probably due to the perceived difficulties associated with coupling of crystallographic and magnetic structures.

3.3 Magnetic phase transition

The temperature dependence of magnetization (M) for two kinds of annealed $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ samples under zero-field-cooled warming (ZFC) and field-cooled cooling (FC) protocols in magnetic field of 0.02 T is shown in Fig. 4. The T_C values of 1:13 phases are listed in Table 1, determined as a peak in dM/dT plots (not shown here). Although the grain size of α -Fe phase in annealed $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ ribbons is very fine, the differences of T_C for two kinds of $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ samples with the same x are only 2–3 K. This indicates that the magnetic coupling between 1:13 phase and α -Fe phase is negligible in melt-spun ribbons. At the same time, thermal hysteresis phenomena exist in two $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ samples, and do not decrease with the increase of α -Fe content. Thus, the excessive Fe will not change the nature of the first order magnetic phase transition in those annealed $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ samples.

Figure 5 shows magnetization–magnetic field (M – H) curves of two kinds of annealed $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ samples in a field change of 0–2 T. Before measurement, the samples were heated to paramagnetic state and cooled to the measuring temperature in zero field in order to ensure a demagnetized sample. Magnetic hysteresis and field-induced metamagnetic transition from PM to FM above T_C of 1:13 phase are clearly observed, which are manifestations of the first order magnetic transition (FOMT). As shown in Fig. 6, the Arrott plots at and above T_C show “S” shape, further confirming that the metamagnetic PM–FM transitions in those samples are of FOMT [13]. In addition, the curvature of Arrott plot

**Fig. 4** Temperature dependence of ZFC and FC magnetizations measured in magnetic field of 0.02 T

can reflect the intensity of FOMT characteristic [14]. For arc melting $\text{LaFe}_{11.6\times 1.1}\text{Si}_{1.4}$ alloy, the Arrott plot's curvature at T_C is higher than that of other three alloys. Therefore, this alloy has the strongest first order characteristic.

3.4 Magnetocaloric properties

In Fig. 5, M – H curves have bending phenomena in the low field range when temperatures are higher than T_C of 1:13 phase. It is from the contribution of soft magnetic α -Fe phase, which is in ferromagnetic state in the measurement temperature range due to its high T_C of ~ 1023 K. By linearly extrapolating between the first large susceptibility stage and the small susceptibility stage, the M of intersection is the magnetization of α -Fe

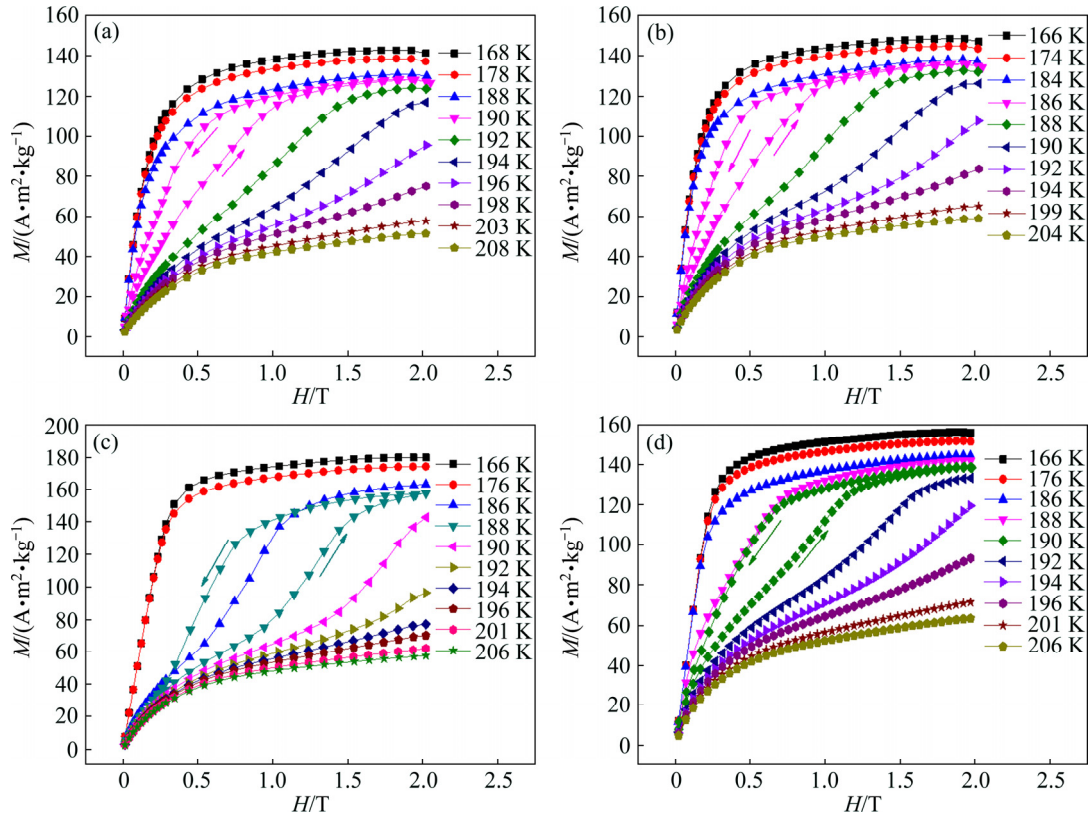


Fig. 5 Isothermal magnetization curves measured in applied magnetic fields from 0 to 2 T: (a) Melt-spun $\text{LaFe}_{11.6 \times 1.1}\text{Si}_{1.4}$ ribbon; (b) Melt-spun $\text{LaFe}_{11.6 \times 1.2}\text{Si}_{1.4}$ ribbon; (c) Arc melting $\text{LaFe}_{11.6 \times 1.1}\text{Si}_{1.4}$ button; (d) Arc melting $\text{LaFe}_{11.6 \times 1.2}\text{Si}_{1.4}$ button

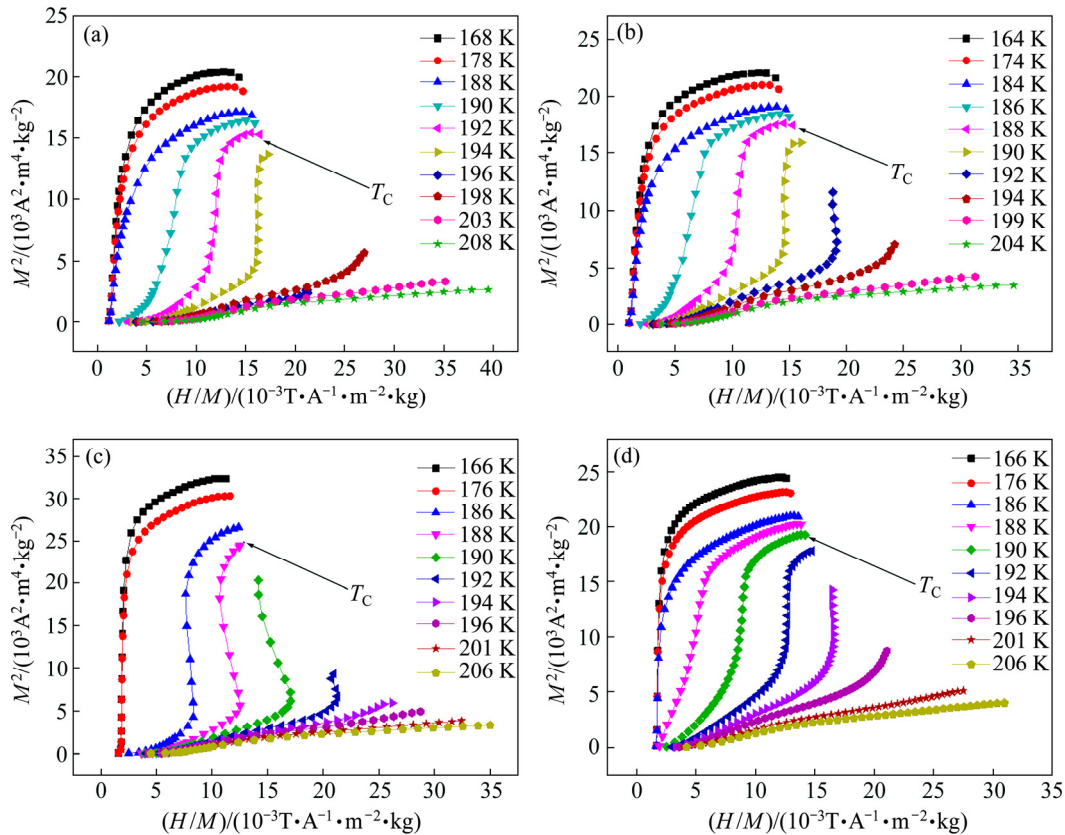


Fig. 6 Arrott plots derived from isothermal magnetization data: (a) Melt-spun $\text{LaFe}_{11.6 \times 1.1}\text{Si}_{1.4}$ ribbon; (b) Melt-spun $\text{LaFe}_{11.6 \times 1.2}\text{Si}_{1.4}$ ribbon; (c) Arc melting $\text{LaFe}_{11.6 \times 1.1}\text{Si}_{1.4}$ button; (d) Arc melting $\text{LaFe}_{11.6 \times 1.2}\text{Si}_{1.4}$ button

phase at the measured temperature. For different samples, with the increase of α -Fe phase content, the magnetization contribution from α -Fe phase also increases. However, α -Fe soft magnetic phase has high T_C , and its magnetization contribution remains almost unchanged in the measured temperature range for the same sample. We can obtain the magnetizations of 1:13 phase at different temperatures in a 2 T applied field via eliminating the magnetization contribution of α -Fe phase. For example, the magnetizations of arc melting $\text{LaFe}_{11.6 \times 1.1}\text{Si}_{1.4}$ and $\text{LaFe}_{11.6 \times 1.2}\text{Si}_{1.4}$ alloys are 180 and 156 $\text{A} \cdot \text{m}^2/\text{kg}$ at 166 K, the magnetization contributions of α -Fe phases are 31 and 44 $\text{A} \cdot \text{m}^2/\text{kg}$, respectively. Thus, the magnetizations of 1:13 phases under 2 T are 149 and 112 $\text{A} \cdot \text{m}^2/\text{kg}$ at 166 K for arc melting alloys with $x=1.1$ and 1.2, respectively. Similarly, the magnetization of 1:13 phase in melt-spun $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ ribbons can be obtained, and the values are only 107 $\text{A} \cdot \text{m}^2/\text{kg}$ at 168 K and 96 $\text{A} \cdot \text{m}^2/\text{kg}$ at 164 K, respectively. The magnetization of 1:13 phase in melt-spun $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ ribbons is lower than that in the corresponding arc melting buttons. According to Clausius–Clapeyron $\Delta S_{\text{Max}} = -(\Delta M \cdot \Delta H_C) / \Delta T$ [15], the negative isothermal magnetic entropy change ($-\Delta S_{\text{Max}}$) is proportional to the magnetization change of 1:13 phase. This predicts that $-\Delta S_{\text{Max}}$ of annealed arc melting $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ buttons should be higher than that of the corresponding melt-spun ribbons.

In fact, the isothermal magnetic entropy change can be calculated by Maxwell equation [16]. The curves of $-\Delta S_{\text{Max}}$ versus temperature in a magnetic field change of 0–2 T are shown in Fig. 7. The peak values of $-\Delta S_{\text{Max}}$ for melt-spun $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ ribbons with $x=1.1$ and 1.2 are 17.22 and 13.2 $\text{J}/(\text{kg} \cdot \text{K})$, respectively, which are obvious smaller than those of the corresponding arc melting $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ alloys, as shown in Table 1, especially at $x=1.1$. The relative cooling power (RCP) is calculated by $-\Delta S_{\text{Max}} \cdot \delta T$ [17], where δT is the temperature full width at half of $-\Delta S_{\text{Max}}$. The RCPs of arc melting $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ buttons with $x=1.1$ and 1.2 are 198.6 and 144.0 J/kg in a field change of 0–2 T, respectively. For melt-spun $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ ribbons, the corresponding values are only 146.2 and 105.6 J/kg , respectively. These results show that the fine grain sized α -Fe phase does not enhance the magnetocaloric properties in melt-spun $\text{LaFe}_{11.6 \times 1.1}\text{Si}_{1.4}$ ribbons. On the contrary, due to the reduced 1:13 phase fraction and increased density of grain boundary, the magnetocaloric effect becomes weak.

4 Conclusions

1) The content of 1:13 phases in the annealed melt-spun ribbons than that in the annealed arc melting buttons with the same composition. The main reason is

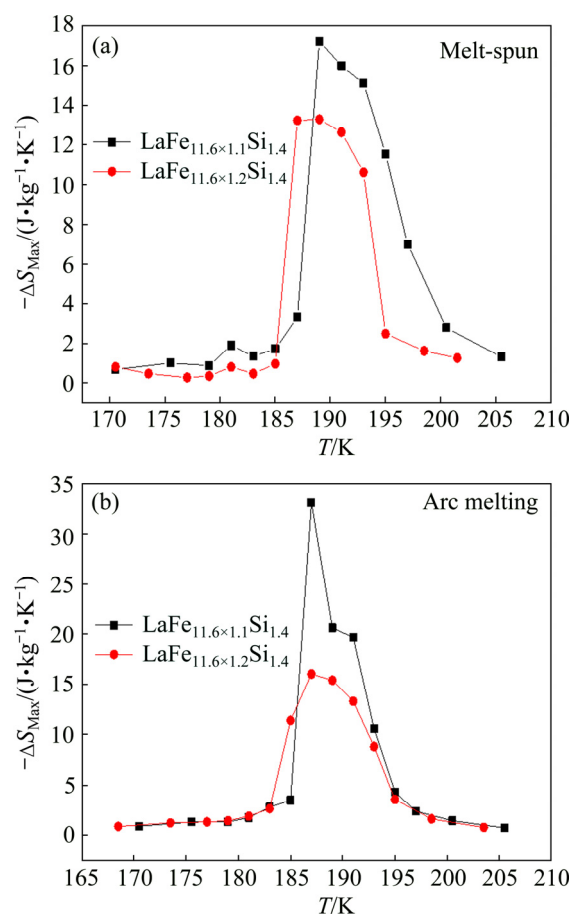


Fig. 7 Comparison of $-\Delta S_{\text{Max}}-T$ curves for $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ samples in magnetic field change of 0–2 T

that the contents of 1:13 and LaFeSi phases in the as-cast melt-spun $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ ribbons are less than those in the corresponding arc melting $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ buttons.

2) The expected magnetic atom coupling between 1:13 phase and α -Fe phase is not observed in annealed melt-spun $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ ribbons. The grain size of excessive α -Fe does not reach the nano-scale, although rapid solidification technology is useful for grain refinement.

3) Magnetocaloric properties of annealed melt-spun $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ ribbons are weaker than those of the corresponding arc melting $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ buttons. At $x=1.1$, the maximum of $-\Delta S_{\text{Max}}$ values for melt-spun ribbon and arc melting buttons are 17.2 and 33.1 $\text{J}/(\text{kg} \cdot \text{K})$ in a magnetic field change of 0–2 T, respectively.

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凝固速度和过量铁对 $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ 合金相形成和磁热性能的影响

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摘 要: 采用 XRD、SEM 和 VSM 等方法研究凝固速度和过量 Fe 对 $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ ($x=1.1, 1.2$) 试样相形成和磁热性能的影响。XRD 研究结果表明, 以 10 m/s 速度甩带制备的铸态 $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ 试样中 LaFeSi 相的含量低于采用电弧熔炼的相同配比铸态 $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ 纽扣试样中 LaFeSi 相的含量, 且在对应热处理后试样中, 甩带试样中的 $\text{La}(\text{Fe}, \text{Si})_{13}$ 相(1:13 相)的含量也更低。SEM 结果表明, 虽然甩带能使热处理后试样中 $\alpha\text{-Fe}$ 相晶粒组织细化, 但并未达到纳米级, 因此, 未观察到 1:13 相和 $\alpha\text{-Fe}$ 相中磁性原子的磁耦合现象。磁热性能研究表明, 经过相同热处理后甩带 $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ 试样在 0–2 T 磁场中的最大磁熵变和相对制冷能力也低于同成分 $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ 纽扣试样的最大磁熵和相对制冷能力。

关键词: $\text{LaFe}_{11.6x}\text{Si}_{1.4}$ 合金; 凝固速率; 显微组织; 磁热性能

(Edited by Wei-ping CHEN)