Reduced Annealing Time and Enhanced Magnetocaloric Effect of $\text{La}(\text{Fe}, \text{Al})_{13}$ Alloy by La-nonstoichiometry and Si-doping

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Abstract

$\text{LaFe}_{13-x}\text{M}_x$ ($M = \text{Si}, \text{Al}$) alloys are promising for use in magnetic refrigeration. However, they require long annealing time (30 days) in order to optimize the magnetocaloric properties. Research has shown that the addition of extra La in off-stoichiometric alloys can greatly shorten the annealing time. Therefore, the purpose of this study is to investigate the influence of the extra addition of La on the annealing properties of a new off-stoichiometric $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x = 0, 0.1, 0.4$) alloys. It was demonstrated that after a 36h annealing time, a large volume fraction of 1:13 magnetocaloric phase was obtained for all alloys. Further microstructural analysis of the off-stoichiometric $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ alloys revealed a facet-like grain morphology. The $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$ and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ alloys were shown to contain large 1:13 phase precipitates separated in a La-rich matrix, while the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.4}$ alloy had a continuous 1:13 phase matrix with a fine dispersion of La-rich precipitates throughout. When the magnetic field varied between 0 and 2 T, the corresponding magnetic entropy change and relative cooling capacity for the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ specimen were determined as 4.58 J/kg K and 173.6 J/kg, respectively. More importantly, the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ alloy displayed only a slight volume change when the meta-magnetic phase transition occurred, which is promising for cyclic use.

Keywords Solidification · Magnetic properties · Heat treatment · Microstructure · Functional alloys

1 Introduction

NaZn_{13} -type $\text{LaFe}_{13-x}\text{M}_x$ ($M = \text{Si}, \text{Al}$) alloys are promising for use in magnetic refrigeration due to their inherent magnetocaloric effect (MCE), low cost and environmentally friendly constituting elements [1–5]. Of particular interest are $\text{LaFe}_{13-x}\text{Si}_x$ ($x \leq 1.8$) alloys which demonstrate a giant MCE, and thus, they have been the focus of a

substantial amount of research [6–9]. The MCE originates from the magnetic phase transition [10]. $\text{LaFe}_{13-x}\text{Si}_x$ alloys go through a first-order itinerant electron metamagnetic (IEM) transition from a paramagnetic (PM) to a ferromagnetic (FM) state, which is accompanied by a negative lattice expansion. Because solid refrigeration is achieved in thermal cycles, relatively large negative lattice expansions result in damage to the materials that are being used [11]. Consequently, a substantial amount of research has gone into improving the cyclic ability of $\text{LaFe}_{13-x}\text{Si}_x$ alloys [12].

In comparison, $\text{LaFe}_{13-x}\text{Al}_x$ alloys display only a comparatively small lattice expansion [13]. Therefore, inner stresses that may originate from the magneto-structural phase transition are reduced, thus making them promising for cyclic use [14]. Unlike $\text{LaFe}_{13-x}\text{Si}_x$ alloys, $\text{LaFe}_{13-x}\text{Al}_x$ alloys go through a first-order itinerant electron metamagnetic (IEM) transition from a paramagnetic (PM) to an antiferromagnetic (AFM) state. As the magnetic field increases, a phase transition from the AFM to ferromagnetic (FM) state is observed. $\text{LaFe}_{13-x}\text{Al}_x$ alloys also have a lower annealing temperature (1173–1273 K) than $\text{LaFe}_{13-x}\text{Si}_x$ alloys (1323–1423 K) because Al possesses a lower melting point than Si [15,

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[16]. Additionally, the working temperature range for magnetic refrigeration of $\text{LaFe}_{13-x}\text{Al}_x$ alloys is comparatively broad, which is beneficial for a refrigerator to perform better during thermal cycling and results in a refrigerator with a greater cooling capacity [17]. Hence, a considerable amount of research has been conducted on $\text{LaFe}_{13-x}\text{Al}_x$ alloys for use in magnetic refrigeration [18–20]. In order to optimize the magnetocaloric effect of $\text{LaFe}_{13-x}\text{Al}_x$ alloys, Dong et al. introduced Si doping to enhance magnetic-elastic coupling [21]. Because $\text{LaFe}_{13-x}\text{Al}_x$ and $\text{LaFe}_{13-x}\text{Si}_x$ alloys have the same crystal structure, $\text{LaFe}_{13-x}\text{Al}_x$ can be doped with Si to reduce the lattice parameter, thereby enhancing magnetic entropy change.

To our knowledge, stoichiometric $\text{La}(\text{Fe}, \text{Al}, \text{Si})_{13}$ alloys require 30 days of annealing to ensure homogenization [22]. This annealing step is necessary to obtain a large volume fraction of the $\text{LaFe}_{13-x}\text{Al}_x$ phase, since as-cast specimens are constituted of only α -Fe prime and $\text{La}(\text{Fe}, \text{Al})_2$ phases [23]. The best technique to reduce annealing time is the melt-spun method, as this refines the α -Fe prime phase which is then easily dissolved into the $\text{LaFe}_{13-x}\text{M}_x$ matrix [24]. Recently, research in off-stoichiometric $\text{La}_{1.7}\text{Fe}_{11.6}\text{Si}_x$ bulk alloys have shown that the addition of extra La greatly shortens the annealing time [25–27]. In fact, in some cases, the annealing time for La-rich $\text{La}_{1+x}(\text{Fe}, \text{Si})_{13}$ ($x=0.7\text{--}1.2$) alloys has been reduced to 3 days [26]. Therefore, it is reasonable to speculate that the addition of extra La in the $\text{LaFe}_{13-x}\text{Al}_x$ alloys is likely to further shorten the annealing time. However, to the best of our knowledge, this has not been reported in the literature.

In this research, $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) alloys with extra La addition and Si doping are fabricated in order to reduce the long annealing time of $\text{LaFe}_{11.6}\text{Al}_{1.4}$ alloy to improve their magnetocaloric properties. In addition, it is expected that the combination of extra La and Si within the microstructure will result in morphological changes which should be investigated. Within this work, the as-cast and annealed microstructure of $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) alloys and their corresponding magnetic properties are systematically studied.

2 Experimental

Homogeneous $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) rod-shaped ingots were prepared in an induction furnace using La (with > 99.5% purity), Fe (with > 99.99% purity), Al (with > 99.99% purity) and Si (with > 99.9999% purity) raw materials. The heat treatment of specimens was carried out in a quartz tube, evacuated up to about 10^{-3} Pa. The $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) ingots were annealed at different temperatures, as listed in Table 1. The annealing temperatures were set based on the annealing temperature

Table 1 $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) specimen annealed at different conditions

Component	Annealing temperature (K)	Annealing time (h)	Microstructure
$\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$	1198	36	α -Fe + La-rich
	1248	36	1:13 + La-rich
	1273	36	1:13 + La-rich + α -Fe
$\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$	1198	36	1:13 + La-rich
	1248	36	1:13 + La-rich + α -Fe
$\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$	1198	36	α -Fe + La-rich
	1248	36	1:13 + La-rich
	1273	36	1:13 + La-rich + α -Fe

range (1198–1273 K) of $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$ alloy. The specimens were annealed for 36 h, followed by water quenching.

Specimen microstructures were observed in a scanning electron microscope (SEM; Phenom XL). The compositional distributions were investigated using energy-dispersive spectroscopy (EDS). Identification of the crystal structure was conducted by X-ray diffraction (XRD; Rigaku, Ultima IV) using $\text{Cu K}\alpha$ radiation at a scan speed of $10^\circ \text{ min}^{-1}$. Magnetic measurements were carried out using a Quantum Design PPMS SQUID vibrating sample magnetometer in magnetic fields up to 2 T. Magnetic property testing was performed on specimens when the α -Fe phase had completely dissolved into the microstructure, as the existence of the α -Fe phase is detrimental to the MCE. From our results, the best annealing temperature for the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$, $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ specimens was 1248 K, 1198 K and 1248 K, respectively. Thermal expansion tests were performed by a thermal dilatometer (DIL 402 Expedit).

3 Results and Discussion

3.1 Microstructure and Phase Analysis

Figure 1 shows the microstructure of as-cast and annealed $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) specimens. The dark grey is the α -Fe prime phase, the light grey is the La-rich phase, and the moderate grey is the $\text{La}(\text{Fe}, \text{Al}, \text{Si})_{13}$ (1:13 phase). According to equilibria, the La-rich phase refers to a combination of $\text{LaFe}_{2-y}(\text{Al}, \text{Si})_y$ and La_5Si_3 . For La–Fe–Al alloys, the La-rich phase refers to $\text{LaFe}_{2-y}\text{Al}_y$, while for La–Fe–Si alloys, it refers to LaFeSi and La_5Si_3 [28, 29].

1:13 phase in $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ specimen forms facet-like grains with sharp edges (Fig. 1f). These grains are separated by the La-rich phase. This morphology is similar to the reported $\text{La}_{1.7}\text{Fe}_{11.6}\text{Si}_{1.4}$ alloy [26]. The 1:13 phase formed both in $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$ (Fig. 1d) and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ (Fig. 1e) displays a facet-like morphology, however,

Fig. 1 a–c SEM (backscattered mode) images of as-cast $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$, $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ specimens, respectively. d–f SEM images of annealed $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$ (1248 K, 36 h), $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ (1198 K, 36 h) and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ (1248 K, 36 h) specimens, respectively. Main phases of $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) alloys are highlighted in the image

unlike $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ specimen no sharp edge grains are revealed. It can also be seen that $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ (Fig. 1e) forms a continuous connected 1:13 phase with a relatively evenly distributed La-rich phase that appears to segregate toward the grain boundaries [30]. Based on the annealed morphology of $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) specimens, it is observed that the annealing time of $\text{La}(\text{Fe}, \text{Al})_{13}$ alloys can be reduced via La-nonstoichiometry and Si-doping.

Figure 2 shows the XRD patterns of specimens annealed at different temperature. For $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$ specimen with annealing temperature of 1198 K, only the strongest peak (110) corresponding to the $\alpha\text{-Fe}$ phase is observed. At this temperature, the 1:13 phase does not appear, which illustrates that the $\alpha\text{-Fe}$ phase has not dissolved to form the expected 1:13 phase. When the annealing temperature is increased to 1248 K, the XRD pattern demonstrates that a large volume fraction of the 1:13 phase is formed.

Interestingly, even after annealing at 1273 K for 36 h, the $\alpha\text{-Fe}$ peak remains in the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ specimen [30]. This can be explained by inverse diffusion interface movement, which results in the coarsening of $\alpha\text{-Fe}$ prime phase, similar behavior is reported in the literature [31].

By comparing SEM and XRD patterns, the optimized heat treatment for each new off-stoichiometric

Fig. 2 XRD patterns of $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) specimens annealed at selected temperatures for 36 h

$\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) alloy can be determined. Because the existence of any $\alpha\text{-Fe}$ phase negatively influences the magnetocaloric effect of $\text{La}(\text{Fe}, \text{Al}, \text{Si})_{13}$ alloys, it is suggested further research should focus on increasing

the 1:13 phase while reducing the α -Fe phase [32]. From the annealing work, the optimized annealing temperatures are determined as 1248 K for $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$, 1198 K for $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$, and 1248 K for $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$. For all three off-stoichiometric alloys, the peaks corresponding to the 1:13 phase move to a slightly larger angle as Si content increases, thus indicating the influence of Si doping on the crystal structure [20].

3.2 Magnetic Properties

This section investigates the magnetic properties of annealed $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) specimens under their optimized annealed conditions. Figure 3 shows the temperature-dependent magnetization curves for the three annealed specimens. Unlike some stoichiometric $\text{LaFe}_{11.4}\text{Al}_{1.6-x}\text{Si}_x$ ($x=0-0.4$) alloys [21], the AFM state is not observed in $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) alloys. However, all specimens undergo the FM-PM transition, indicating the influence of the secondary phase on the phase transition by the addition of extra La [26]. Although the AFM state is not observed, it does not mean the 1:13 phase does not exhibit an FM-AFM transition. Actually, the FM-AFM transition is closely connected with the Si/Al ratio. For $\text{LaFe}_{11.4}\text{Al}_{1.6-x}\text{Si}_x$ alloys, the FM-AFM state occurs when the Si/Al ratio (0.22/1.38) is relatively small [21]. And thus, for $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ alloys, there exists a FM/PM-AFM/PM boundary which indicates the alloy has an excellent

cooling capacity with only a small structural change. This has been systematically analyzed in other alloys such as $\text{MnCo}_{1-x}\text{Zn}_x\text{Ge}$ [33].

Figure 3 illustrates the influence of Si content on the magnetization range and Curie temperature of $\text{LaFe}_{11.4}\text{Al}_{1.6-x}\text{Si}_x$ ($x=0-0.4$) alloys. It is known that the occurrence of a magneto-structural transition requires a certain relaxation time [34]. The time taken to lose the materials magnetic characteristics has a close relationship with the derivative of the M - T curve. The slope of M - T curve for the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ specimen is lower than the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$, so the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ specimen actually requires a lower activation energy.

It is determined from the derivative M - T curve in Fig. 3b that the Curie temperatures (T_C) of annealed $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$, $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ specimens were 195 K, 200 K and 181 K, respectively. Clearly, the variation of T_C is consistent with Si doping. Since Al atoms have a larger size than Si atoms, the replacement of Al by Si causes the lattice to shrink. And therefore, enhancing Fe-Fe coupling results in a decrease in the T_C [35, 36]. As for the small increase of T_C for the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ specimen, it is assumed that the continuous morphology and different volume fraction of 1:13 phase play an important factor [26].

Figure 4a-c shows the isothermal magnetization curves for three $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) specimens. When the magnetic field is increased at low temperatures below T_C , the magnetization saturates immediately, clearly

Fig. 3 M - T curves for annealed $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$ (1248 K, 36 h), $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ (1198 K, 36 h) and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ (1248 K, 36 h) specimens under a magnetic field of 0.02 T **a**. The corresponding derivative curve used to determine the Curie temperature of the specimens **b**

Fig. 4 **a–c** Isothermal magnetization curves of annealed $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$ (1248 K, 36 h), $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ (1198 K, 36 h) and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ (1248 K, 36 h) specimens, respectively. **d–f** Corresponding magnetic entropy change

demonstrating the FM phase characteristics of the specimens. It is known that the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$ specimen demonstrates a second-order magnetic transition. In this case, in the vicinity of T_C , the magnetization still shows the FM phase characteristics while the saturation decreases.

However, for the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ specimens, as the temperature increases in the vicinity of T_C , the magnetization gradually increases as magnetic field increases. This indicates there is a weak IEM magnetic transition from the PM to the FM state. These results illustrate that Si doping encourages the occurrence of the IEM transition, which is in consistent with the research of Dong et al. [21].

The magnetic entropy change ΔS_M is calculated from the isothermal magnetization curves (M - T) using the Maxwell relationship:

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

where H is the applied magnetic field. Figure 4d–f shows ΔS_M as a function of temperature for all three specimens. The maximum ΔS_M values of the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$, $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ specimens under a varying magnetic field (0 T to 2 T) were 3.49 J/kg K, 4.58 J/kg K and 4.39 J/kg K, respectively. The maximum ΔS_M values obtained for the off-stoichiometric $\text{La}_{1.7}(\text{Fe}, \text{Al}, \text{Si})_{13}$ alloys are similar to that of stoichiometric

$\text{La}(\text{Fe}, \text{Al}, \text{Si})_{13}$ alloys [5, 23]. It can also be seen from the ΔS_M vs temperature curves that the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$ and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ specimens have a broader working temperature range.

When considering an ideal thermodynamic cycle, the relative cooling power (RCP) characterizes magnetocaloric materials and determines their refrigerant capacity. The RCP, based on the magnetic entropy change, is calculated from $(\Delta S_M)_{\max}$ and δT_{FWHM} by the equation:

$$\text{RCP} = -(\Delta S_M)_{\max} \times \delta T_{\text{FWHM}}. \quad (2)$$

where δT_{FWHM} is the full width at half-maximum of the ΔS - T curve. It can be seen from δT_{FWHM} curves that the ΔS_M curve becomes narrower as Si doping increases. As shown in Fig. 5, the maximum refrigerant capacity of $\text{La}_{1.7}(\text{Fe}, \text{Al}, \text{Si})_{13}$ alloys doped with a small amount Si under a magnetic field of 2 T is 173.6 J/kg. Under the same magnetic field, $\text{La}(\text{Fe}, \text{Si})_{13}$ compounds have a lower RCP below ~ 150 J/kg [17, 37] and Ni–Mn–Co–Sn alloys have an RCP of ~ 50 J/kg [38]. Therefore, the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ alloy demonstrates very promising characteristics for use in practical magnetic refrigeration applications [39].

Fig. 5 Relative cooling power (RCP) for an applied magnetic field of 0–2 T **a** and δT_{FWHM} of all three specimens **b**

3.3 Thermal Expansion

When the meta-magnetic phase transition occurs, it is also accompanied by a magnetovolume change. Hu et al. [11] have shown that the isotropic volume can change by $\sim 1.3\%$. In general, the magnetocaloric effect is positively related to the amount of magnetovolume change, in another word, the larger the bulk expansion (shrinkage), the greater the magnetic entropy change. Therefore, for alloys to achieve large magnetic entropy change, a large volume change during the phase transition is expected. However, when the magnetovolume effect occurs it is accompanied by a large internal stress, which is demonstrated in Fig. 6a.

Glushko et al. [39] calculated the inner stress (σ_V) using the equation:

$$\sigma_V = K\varepsilon_V = \frac{E}{3(1-2\nu)} \frac{\Delta V}{V} = \frac{E}{1-2\nu} \frac{\Delta L}{L}. \quad (3)$$

where K is bulk modulus, ε_V is the deformation, E is the Young's modulus, ν is the Poisson's ratio, $\frac{\Delta V}{V}$ is the relative volume change and $\frac{\Delta L}{L}$ is the linear thermal expansion. Using this equation, the inner stress for $\text{LaFe}_{11.8}\text{Si}_{1.2}$ alloys is estimated to reach 2.2 GPa. Since the $\text{La}(\text{Fe}, \text{Si})_{13}$ phase is rather brittle, $\text{La}(\text{Fe}, \text{Si})_{13}$ alloys will fracture after several magnetic refrigeration cycles, thus leading to poor practical use [35]. Therefore, it is essential to understand how thermal expansion affects magnetocaloric materials. For most compounds, such as in $\text{LaFe}_{11.4}\text{Si}_{1.6}$ alloys [12], unless a solid-phase transition occurs, there is usually a continuous positive thermal expansion as the surrounding temperature rises. In this case, a positive expansion phase and a negative expansion phase are required to achieve zero expansion;

therefore, composites with a multi-phase microstructure are expected.

Thermal expansion tests were performed by a thermal dilatometer ($\Delta L/L(T = 225 \text{ K})$ was determined as reference). Figure 6b shows the linear thermal expansion $\Delta L/L$ of all specimens. The average coefficient of thermal expansion (CTE) can be calculated by the relationship:

$$\Delta \text{CTE} = \Delta L(T_1) - \Delta L(T_2) / (L \cdot |T_1 - T_2|). \quad (4)$$

where T is the temperature. The CTE of $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$, $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ specimens was obtained as $-4.3 \times 10^{-5} \text{ K}^{-1}$, $-2.1 \times 10^{-5} \text{ K}^{-1}$ and $-7.8 \times 10^{-5} \text{ K}^{-1}$, respectively. Compared with the $\text{La}(\text{Fe}, \text{Si})_{13}$ alloys mentioned above, the CTE of $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) specimens is comparatively low. There are two possible reasons for the lower CTE. Firstly, $\text{La}(\text{Fe}, \text{Al})_{13}$ has a low CTE [40], and the current specimens have a similar composition to $\text{La}(\text{Fe}, \text{Al})_{13}$, which determines the lower CTE of current specimens. In addition, $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) alloys have a dual phase (1:13 phase/La-rich phase) microstructure which also reduces its CTE. Secondly, it is owed to the influence of Si doping, which brings about AFM-FM magnetic phase transition. The differences of CTE between each alloys may be originated from the different microstructure, more precisely, the different connections between the 1:13 functional phase and the La-rich phase, as shown in Fig. 1. The $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ specimen possesses a continuous 1:13 matrix with small distributed La-rich precipitates throughout and shows the smallest change in CTE with increasing temperature, whereas the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$ and the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ specimens have large 1:13 grains which are separated by La-rich channels. Thus, both specimens

Fig. 6 Sketch map of the influence of thermal expansion, which causes internal stress, on cyclic use for multi-phase $\text{LaFe}_{13-x}\text{M}_x$ ($M=\text{Si}, \text{Al}$) alloys when a thermal-induced phase transition occurs **a**. Temperature-dependent thermal expansion of annealed $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$ (1248 K, 36 h), $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ (1198 K, 36 h) and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_1\text{Si}_{0.4}$ (1248 K, 36 h) specimens **b**

have a wider range of CTE with increasing temperature, clearly demonstrating the influence of the microstructure on the CTE.

In addition, combining the thermal expansion results with the ΔS_M curve, it is found that a small linear thermal expansion can introduce a comparatively large benefit for the MCE.

4 Conclusions

In this work, the microstructure and magnetic properties of La-rich Si-doping off-stoichiometric $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) alloys for under-optimized annealing conditions are studied. The main conclusions are as follows:

1. The annealing time for $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) alloys has been largely reduced from the conventional 30 days to 36 h.
2. The microstructure of off-stoichiometric $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ alloys display facet-like grains. The grains of $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4}$ and $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ specimens are shown to be separated by a La-rich matrix, while the grains of $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ are connected and continuous.
3. Si doping influences the magnetic entropy change, relative cooling capacity and the thermal expansion of annealed $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.4-x}\text{Si}_x$ ($x=0, 0.1, 0.4$) specimens. As the applied magnetic field is changed from 0 to 2 T, the $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ specimen achieves a ΔS_M of 4.58 J/kg K and a corresponding relative cooling capacity of 173.6 J/kg. Furthermore, $\text{La}_{1.7}\text{Fe}_{11.6}\text{Al}_{1.3}\text{Si}_{0.1}$ exhibits a low coefficient of thermal expansion which is beneficial for the magnetocaloric effect.

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