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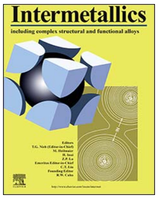

Enhanced magnetocaloric properties in off-stoichiometric $La_xFe_{11.5}Si_{1.5}$ alloys

G.F. Wang[a,*], Z.R. Zhao[b], T. Jing[b], Y.F. Li[b], Q. Ma[b], X.F. Zhang[b,**]

[a] Key Laboratory of Integrated Exploitation of Bayan Obo Multi-Metal Resources, Inner Mongolia University of Science and Technology, Baotou, 014010, China
[b] School of Science, Inner Mongolia University of Science and Technology, Baotou, 014010, China

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ABSTRACT

In this paper, we report on the microstructure and magnetocaloric effect in off-stoichiometric $La_xFe_{11.5}Si_{1.5}$ alloys. The X-ray diffraction and microstructural analysis indicate that the atomic ratio of Fe:Si in the main 1:13 phase is modified by adding excessive La. The off-stoichiometric alloys exhibit lower Curie temperatures and larger thermal hysteresis when comparing with the $x = 1.0$ alloy. The maximum isothermal entropy change is enhanced by 15% when the excessive La content is $x = 1.2$. The present study offers an effective and simply way to improve the magnetocaloric effect in such La-Fe-Si alloys.

1. Introduction

In recent years, the cubic $NaZn_{13}$-type $LaFe_{13-x}Si_x$ alloys have been paid much attention due to their giant magnetocaloric effect (MCE) which is beneficial to the magnetic refrigeration application. It is a matter of fact that pure binary intermetallic $LaFe_{13}$ alloy does not exist due to a positive formation enthalpy between La and Fe. The addition of Si plays important role for stabilizing the $NaZn_{13}$-type structure. In the past decade, a number of studies on structural, magnetic and magnetocaloric properties of such $NaZn_{13}$-type alloys have been reported [1–12]. Han et al. reported that the $LaFe_{13-x}Si_x$ alloys crystalized in the cubic $NaZn_{13}$-type structure (space group $Fm\bar{3}c$) for $1 \le x \le 2.6$ and in the tetragonal $Ce_2Ni_{17}Si_{13}$-type structure (space group $I4/mcm$) for $3.2 \le x \le 5$, and a mixture of two phases existed in the range $2.6 \le x \le 3.2$ [13]. The ratio of Fe:Si does not only affect on the crystal structure but also on the Curie temperature and MCE in $LaFe_{13-x}Si_x$ alloys. Generally, it was found that with increasing Si concentration the Curie temperature increased and the MCE decreased. For instance, Gutfleisch et al. found that the Curie temperature (T_C) increased from 195 K to 231 K and the maximum isothermal entropy change for a field change of 5 T decreased from 31 J/kg K to 10.3 J/kg K when x changed from 1.2 to 1.8 in $LaFe_{13-x}Si_x$ melt-spun ribbons [14].

The giant MCE in $LaFe_{13-x}Si_x$ alloys originated from first-order phase transition (FOPT) which only took place for the Si content $x \le 1.6$, whereas, the nature of the transition belonged to second-order phase transition for $x > 1.6$ [8,14–16]. The magnetic and magnetocaloric properties of $LaFe_{13-x}Si_x$ alloys were also influenced by the substitution of Fe with other elements, such as Mn and Co. The presence of Mn and Co played different roles in changing the magnetic and magnetocaloric properties. The T_C was reduced and the MCE was slightly changed by the Mn-doping [17]. However, the T_C was improved and the MCE was significantly reduced by the Co-doping [18]. The substitution of La with other rare-earth elements (such as Ce, Pr and Nd) led to a decrease of the T_C but slight influence on MCE [19].

In the present work, the influence of La-excess on magnetic properties and magnetocaloric effect in off-stoichiometric $La_xFe_{11.5}Si_{1.5}$ alloys have been investigated. There are two reasons for performing this study. On one hand, a mount of La would evaporate during the melting process due to its low melting point. Adding excessive La is expected to compensate the consumption of La and further to avoid the formation of α-Fe phase. On the other hand, a single $NaZn_{13}$-type phase is hardly obtained in $LaFe_{13-x}Si_x$ alloys, especially when the Si content is low. Another secondary phase LaFeSi is expected to be formed when more excessive La is introduced, which would lead to the reduction of Si in the main phase and an enhancement of MCE.

2. Experimental

Buttons with nominal compositions of $La_xFe_{11.5}Si_{1.5}$ ($x = 1.0$, 1.1, 1.2 and 1.3) were prepared by high frequency induction melting the mixtures of raw materials (La: 99.8 wt%, Fe: 99.9 wt%, Si 99.9 wt%) in an argon atmosphere. In order to obtain homogeneous alloys, each button was turned and remelted four times after removing the surface layer. The as-cast buttons were sintered at 1423 K for 100 h under

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[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: gaofengwang1982@gmail.com (G.F. Wang), xuefeng367@163.com (X.F. Zhang).

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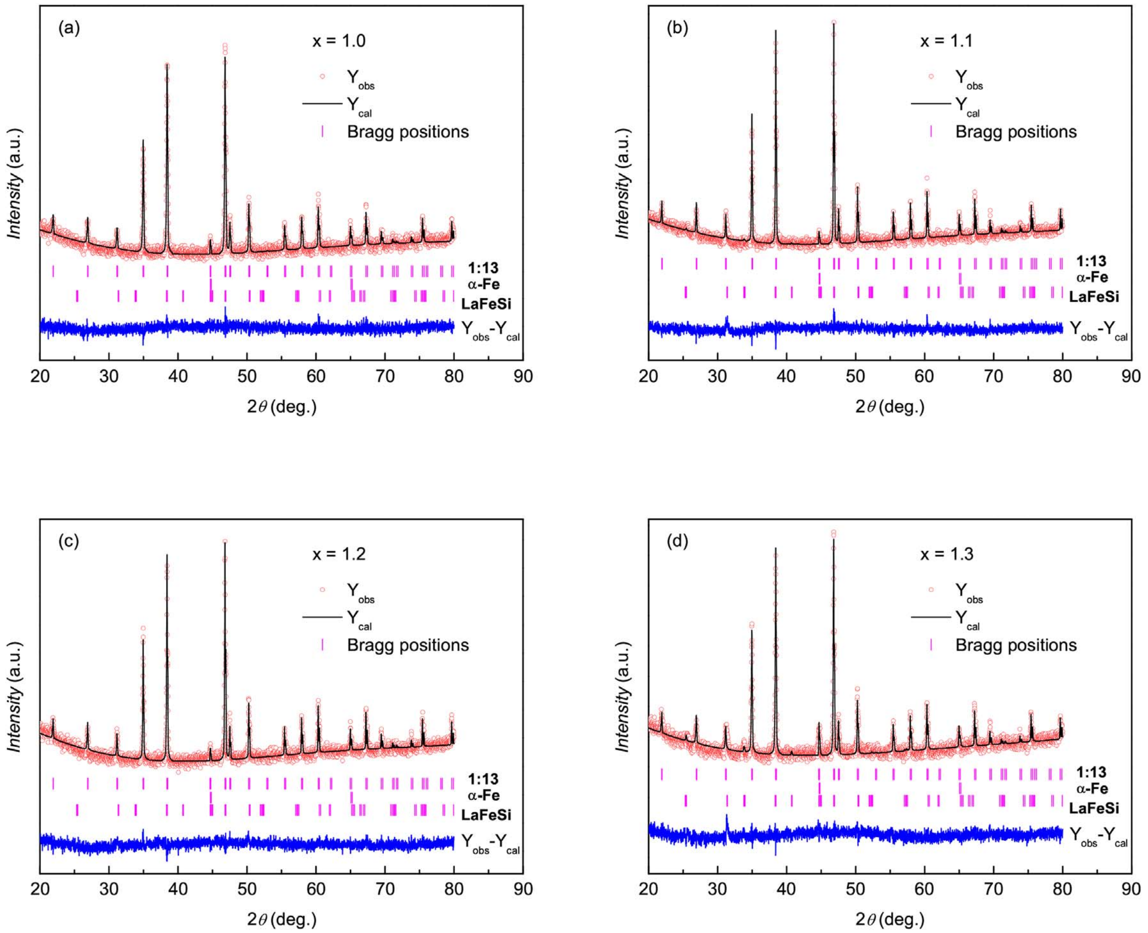

Fig. 1. XRD patterns of $La_xFe_{11.5}Si_{1.5}$ alloys measured at room temperature. Red circles: experimental data. Black line: calculated pattern. Pink ticks: positions of the Bragg reflections for the 1:13 main phase, α-Fe phase and LaFeSi phase. Blue line: difference between the experimental and calculated patterns. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

protection of argon gas and subsequently cooled freely to room temperature. Crystal structure of the alloys was characterized by X-ray diffraction (XRD, PANalytical X'Pert Powder) with Cu-K_α radiation. Microstructure was observed in backscattered electron (BSE) mode by scanning electron microscope (SEM, Supra55, Zeiss). Energy dispersive spectroscopy (EDS) measurement was performed to determine the chemical composition of each phase. Magnetization as a function of temperature at a low magnetic field (isofield $M-T$ curves) and magnetization as a function of magnetic field at different temperatures (isothermal $M-H$ curves) were measured using a vibrating sample magnetometer (VSM, Versalab).

3. Results and discussion

Fig. 1 displays the XRD patterns measured at room temperature for $La_xFe_{11.5}Si_{1.5}$ alloys. The Rietveld refinements were carried out for the patterns using FULLPROF program. The resulting parameters and corresponding reliability factors are summarized in Table 1. It is seen that the lattice parameter remains almost unchanged for the studied alloys. Impurities of α–Fe and LaFeSi are also observed in the patterns. As one can see that the intensity of Bragg peak ($2\theta \approx 44.6°$) of α–Fe phase for $x = 1.1$ is the weakest among the studied alloys and it is the strongest for $x = 1.3$. Namely, the former alloy contains the least amount of α–Fe phase and the latter alloy contains the most amount of α–Fe phase. Another secondary LaFeSi phase is obviously visible in the $x = 1.3$ alloy. Details of phase construction obtained from analysis of the XRD patterns are listed in Table 1.

The microstructural phase construction and the composition of the main 1:13 phase in the alloys was characterized by electron back scattered diffraction and energy dispersive spectrometer, as shown in Fig. 2. In Fig. 2, the gray background indicates the main 1:13 phase, the black and white zones stand for α–Fe and LaFeSi phases, respectively. All alloys contain α–Fe phase which is in agreement with the XRD result. The LaFeSi phase is visible not only in the $x = 1.1$ and 1.3 alloys but also in the $x = 1.2$ alloy (indeed even for the $x = 1.0$ alloy, small crystalline LaFeSi grains may exist) which is inconsistent with that observed in XRD patterns. It is due to the fact that the minor amounts of LaFeSi phase are out of the resolution of the XRD technique.

Table 1
Values of lattice constant (a), profile factor (R_p), weighted profile factor (R_{wp}), global chi-square (χ^2), phase fractions of the main 1:13 phase, α-Fe and LaFeSi for the $La_xFe_{11.5}Si_{1.5}$ alloys.

Composition	a (nm)	R_p (%)	R_{wp} (%)	χ^2	1:13 phase	α-Fe	LaFeSi
$x = 1.0$	1.1471	2.34	2.92	1.34	98.2%	1.8%	0
$x = 1.1$	1.1470	2.37	3.00	1.37	97.4%	1.9%	0.7%
$x = 1.2$	1.1472	2.50	3.15	1.40	98.1%	1.9%	0
$x = 1.3$	1.1473	2.52	3.19	1.49	94.1%	4.23%	1.7%

In $LaFe_{13-x}Si_x$ system, the La atoms occupy only the 8a site, the Fe atoms occupy 8b and 96i sites, and the Si atoms occupy preferentially the 96i site rather than the 8b site [20]. Therefore, the addition of La would change the composition of the main phase since there is no extra 8a position for the additional La atoms in the cubic $NaZn_{13}$-type structure. Moreover, the composition of the main phase would be also modified by the existence of the secondary phases. Assuming that all La