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Measurements of Magnetocaloric Effect in $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Al_x$ ($x = 0.1$, 0.2, 0.3) Alloys

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In the present work, phase constitution and thermomagnetic properties of $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Al_x$ (where $x = 0.1$, 0.2, 0.3) alloys were investigated. Ingot samples were obtained by arc-melting under the low pressure of Ar atmosphere. Subsequently samples were annealed at 1323 K for 15 days. X-ray diffraction of all samples revealed coexistence of two crystalline phases dominant La(Fe,Si)$_{13}$-type and minor bcc α-Fe. Furthermore, the magnetic measurements at various temperatures allowed to study the Curie temperature, magnetic entropy changes and relative cooling power.

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1. Introduction

Magnetocaloric effect (MCE) is defined as a cooling or heating of magnetic material under the change of external magnetic field. MCE was discovered by Warburg in the 80's of XIX century [1]. In 1997, Pecharsky and Gschneidner Jr. have revealed the giant magnetocaloric effect near room temperature in $Gd_5Si_2Ge_2$ [2]. For this alloy the magnetic entropy change $|\Delta S_M|$ reaches 18.6 J/(kg K) under the change of external magnetic field ≈5 T, at 276 K. High content of Gd and very restrictive processing conditions result in high price of this type of alloys. Therefore they were not commercially utilized as an active regenerators in magnetic refrigerators [3]. More cheaper group of promising magnetocaloric materials are Fe-based alloys. Especially La(Fe,Si)$_{13}$-type alloys reveal high $|\Delta S_M|$ reaching up to 31 J/(kg K) at ≈185 K. Furthermore, it was shown that the Curie temperature T_C can be tailored in the range from 185 to 330 K. The $|\Delta S_M|$ and T_C parameters strongly depend on the chemical composition and processing technique [4–8]. Relatively low price, estimated to ≈8 euro/kg seems to be promising for commercial application. Here the formation of single pseudobinary fcc La(Fe,Si)$_{13}$-phase of $NaZn_{13}$-type structure is responsible for good magnetocaloric properties [9]. A long time annealing of as-cast dendritic alloy at 1323 K is crucial to obtain homogeneous single phase structure [10]. In the present work results of Al addition on formation of La(Fe,Si)$_{13}$-type phase and its influence on magnetocaloric effect, Curie temperature and cooling capacity were studied.

2. Samples preparation and experimental method

$LaFe_{11.14}Co_{0.66}Si_{1.2-x}Al_x$ (where $x = 0.1$, 0.2, 0.3) alloys were prepared by arc-melting of high purity elements under the low pressure of Ar. In order to compensate loses of La during arc-melting, 5 wt.% excess of La was used. The ingot samples were remelted several times to ensure homogeneity. Subsequently samples were annealed in quartz tubes under Ar atmosphere at 1323 K for 15 days. XRD data were collected using Bruker D8 Advance diffractometer with Cu K_α radiation. X-ray diffractometry was supported by the Rietveld analysis using PowderCell 2.4 package [11]. The Curie temperature of prepared samples was investigated in external magnetic field 0.01 T using the Faraday balance with temperature step 0.5 K. Magnetocaloric studies were carried out using LakeShore 7400 rev A VSM vibrating sample magnetometer equipped with 2 T magnet over the temperature range of 180–390 K.

3. Results and discussion

In all cases the XRD studies of annealed specimens revealed coexistence of two crystalline phases: the major La(Fe,Si)$_{13}$-type phase and α-(Fe,Co) (Fig. 1). For samples with Al content $x = 0.1$ small fractions of pure La and $LaSi_2$ were detected. In case of specimen with Al content $x = 0.3$ small amount of LaSi phase was observed. The major phase was marked by the Miller indexes corresponding to appropriate crystallographic planes. Furthermore a shift of XRD peaks to lower angles with increase of Al addition was observed. The Rietveld analysis revealed that expected fcc $NaZn_{13}$-type phase reaches above 87 vol.% for investigated samples. The lattice constants a calculated for the $NaZn_{13}$-type phase were 11.4801, 11.4863 and 11.4889 Å, respectively, for $x = 0.1$, $x = 0.2$ and $x = 0.3$. The a parameter of the α-(Fe,Co) phase (2.86 Å) did not change with the alloy composition. In the unit cell of the La(Fe,Si)$_{13}$-type phase, the La atoms occupy 8a positions, while Fe atoms prefer two crystallographic sites 8b (Fe(I)) and 96i (Fe(II)). Furthermore, Si, Co and Al additions replace Fe(II) in 96i positions [12]. Moreover, the XRD studies have shown that the aluminium addition promotes formation of the La(Fe,Si)$_{13}$-type phase and decrease of the volume fraction of α-Fe. This phenomenon can be explained by the

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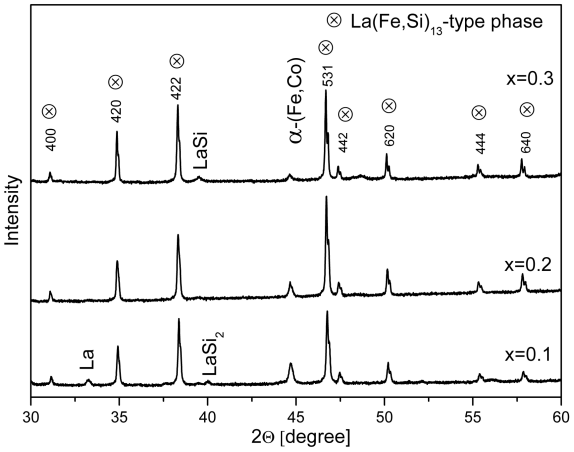

Fig. 1. XRD patterns measured for different alloys $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Al_x$ ($x = 0.1, 0.2, 0.3$).

change from positive to negative enthalpy of mixing in the $LaFe_{13}$ phase, thus leading to its stabilization [13]. More detailed results of the Rietveld analysis are presented in Table I, where recognized phases were marked by symbols β = La(Fe,Si)$_{13}$-type phase and $\alpha = \alpha$-Fe.

TABLE I

Results of Rietveld analysis carried out for XRD patterns measured for $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Al_x$ (where $x = 0.1$, 0.2, 0.3) alloys (β = La(Fe,Si)$_{13}$-type, $\alpha = \alpha$-Fe).

Al content x	Phase	Fraction [vol. %]	Lattice constant a [Å]
0.1	β/α	87/13	11.480/2.86
0.2	β/α	91/9	11.486/2.86
0.3	β/α	96/4	11.489/2.86

The normalized magnetization vs. temperature $M(T)$ dependences with corresponding first derivative $\mathrm{d}M/\mathrm{d}T$ were shown in Fig. 2. Values of the Curie temperature evaluated from $\mathrm{d}M/\mathrm{d}T$ curves reach 264, 265 and 266.5 K, respectively, for $x = 0.1$, 0.2 and 0.3 alloys. Similar results were observed in previous studies [14–16], where the increase of T_C and rise of lattice constant a with the Al addition were shown. In present studies increase of lattice parameter together with the increase of T_C was also observed. However, as we have shown in [15] the larger amount of Al addition caused significant change of the lattice constant of the La(Fe,Co,Si, Al)$_{13}$ phase, which resulted in a significant rise of T_C. In the present work, a low content of Al results in relatively small change of a and consequently small increase of T_C value. The Curie point value depends on the Fe–Fe interactions [17] in this type of alloys. It was shown in [12] that Al atoms occupy 96i positions and cause local structural disorder in La(Fe,Si)$_{13}$-type unit cell. Substitution of Fe by Al may lead to strengthening of Fe–Fe interactions due to change of distances between nearest neighbours of Fe atoms in La(Fe,Si)$_{13}$-type structure.

In order to determine magnetic entropy changes $|\Delta S_\mathrm{M}|$ in the investigated alloys, magnetic field dependences of

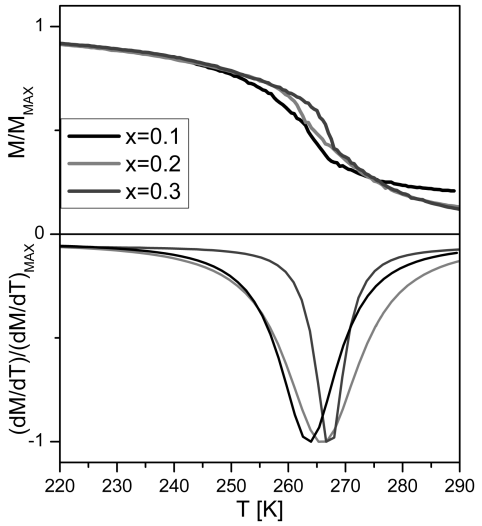

Fig. 2. Temperature dependences of magnetization and their first derivative for all investigated samples.

magnetization in the wide range of temperatures were measured. The $|\Delta S_\mathrm{M}|$ were calculated using Maxwell thermodynamic relation [18]:

$$\Delta S_\mathrm{M}(T,H) = \int_0^H \left(\frac{\delta M(T,H)}{\delta T}\right)_H \mathrm{d}H, \qquad (1)$$

where T — temperature, $M(T,H)$ — magnetization, H — external magnetic field.

The temperature dependences of $|\Delta S_\mathrm{M}|$ calculated for different changes of external magnetic field ΔH are shown in Fig. 3. Characteristic maxima of $|\Delta S_\mathrm{M}|$ around Curie points were revealed for all investigated samples. For the change of external magnetic field ΔH of 2 T the magnetic entropy change $|\Delta S_\mathrm{M}|$ reaches 3.20 J/(kg K), 2.84 J/(kg K) and 2.46 J/(kg K) for $x = 0.1$, $x = 0.2$ and $x = 0.3$, respectively. $|\Delta S_\mathrm{M}|$ values obtained in present studies are almost four times lower than those obtained for La(Fe$_{0.87}$Mn$_{0.02}$Si$_{0.11}$)$_{13}$, reaching ≈16 J/(kg K) [19]. Furthermore, the increase Al in alloy composition causes the decrease of $|\Delta S_\mathrm{M}|$. Similar effect was revealed by Shen et al. [14], where such decrease was attributed to the weakening of the itinerant electron metamagnetic transition with an increase of Al addition. Symmetrical shapes of temperature dependences of $|\Delta S_\mathrm{M}|$ suggest second order phase transition from ferro- to paramagnetic state.

Temperature dependences of magnetic entropy change allowed to calculate relative cooling power (RCP), which was determined using the relation [20]:

$$\mathrm{RCP} = -\Delta S_{\mathrm{M\,max}} \times \delta T_\mathrm{FWHM}, \qquad (2)$$

where RCP is the cooling power, $\Delta S_{\mathrm{M\,max}}$ is the maximum of magnetic entropy change and δT_FWHM a full width at half maximum of ΔS_M temperature dependence.

The calculated values of relative cooling power (RCP) and cooling capacity (RC) are collected in Table II. RCP values decrease with increase of Al addition in the alloy

TABLE II

Values of cooling power calculated for $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Al_x$ (where $x = 0.1$, 0.2, 0.3).

Al content x	$\mu_0\Delta H$ [T]	δT_{FWHM} [K]	RCP [J/kg]
0.1	1	16	20
	2	19	61
0.2	1	17	19
	2	19	54
0.3	1	16	15
	2	19	47

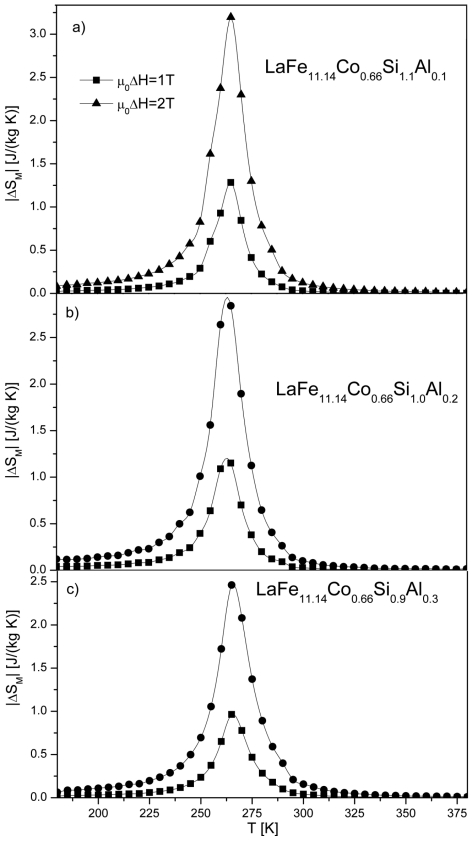

Fig. 3. The magnetic entropy changes $|\Delta S_{\mathrm{M}}|$ vs. temperature calculated for different changes of external magnetic field ΔH up to 2T for the $LaFe_{11.14}Co_{0.66}Si_{1.2-x}Al_x$ (where $x = 0.1$, 0.2, 0.3).

composition. The highest RCP were obtained for the $LaFe_{11.14}Co_{0.66}Si_{1.1}Al_{0.1}$ alloy and are much lower to this obtained for $La(Fe_{0.87}Mn_{0.02}Si_{0.11})_{13}$ alloy [19].

4. Conclusions

It was shown in the present work that the Al addition to the $LaFe_{11.14}Co_{0.66}Si_{1.2}$-based alloy causes expansion of lattice parameter with the increase of the Curie temperature. Additionally increase of Al content in alloy composition causes decrease of magnetic entropy change and cooling power. Decrease of these parameters was attributed to the weakening of itinerant electron metamagnetic phase transition with an increase of Al content in alloy.

Acknowledgments

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