EFFECT OF Al CONTENT ON THE ORDER OF PHASE TRANSITION AND MAGNETIC ENTROPY CHANGE IN $LaFe_{11}Co_{0.8}(Si_{1-x}Al_x)_{1.2}$ ALLOYS

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Abstract

The comparative studies of the effect of partial substitution of Al by Si on the structure and magnetic entropy change in $LaFe_{11}Co_{0.8}(Si_{1-x}Al_x)_{1.2}$ alloys produced by arc-melting followed by long time annealing at 1323K were performed. The X-ray diffraction analysis revealed almost single phase composition of annealed samples. The high intensity synchrotron radiation was used for studying the thermal evolution of lattice constant of the $La(Fe,Co,Si)_{13}$ phase. Furthermore, calculations of temperature dependences of Landau coefficients were used to reveal changes in the character of phase transformation at around the Curie temperature.

Keywords: phase transition, XRD, magnetostructural transformation, magnetic properties

1. Introduction

Although the magnetocaloric effect was well known and utilized in cryogenics for obtaining low temperatures, it has driven much attention over the last two decades due to the discovery of materials showing giant magnetocaloric effect in the vicinity of room temperature. The promising example of such materials is the $Gd_5Si_2Ge_2$ alloy [1], where the magnetic entropy change ΔS_M measured under the alteration of magnetic field $\mu\Delta H$ of 5T reaches 18.5 J(kg K)$^{-1}$ at 276K. The magnetocaloric effect in this compound has his origin in the first order phase transition occurring at around the Curie point, which intensifies the magnetic entropy change [1]. A major drawback of this alloy is relatively high cost of manufacturing. A serious disadvantage (apart from the fact that the alloy is composed of expensive elements) is that a small amount of impurities can significantly affect their performance [2]. Furthermore, the T_C value is rather low for commonly used refrigeration machines. Therefore further intensive studies were focused on search for alloys having possibilities of more flexible change of T_C, high ΔS_M and low costs. Relatively high magnetic entropy change at low magnetic fields was observed for Pr-Fe-type alloys [3]. However good candidate for the room temperature magnetic refrigeration seems to be La-Fe-Si alloy system, where the suitable admixture of constituent elements allows to control the temperature range where the effect occurs [4-6]. Depending on the composition and annealing conditions these alloys form various stable crystalline phases. In order to obtain high magnetocaloric effect a formation of single $NaZn_{13}$-type cubic phase (of the space group Fm3c) [7, 8] is highly preferred. Furthermore the T_C and ΔS_M can be tuned by the alloy composition [9-11]. In the $LaFe_{11.8}Si_{1.2}$ alloy the maximum magnetic entropy change can reach 31 J (kg K)$^{-1}$ at ~200K for $\mu_0\Delta H$ of 5T [12]. In this case the magnetocaloric effect is also related both to

the transition from ferro- to paramagnetic state and to the fact that the elementary cell undergoes a transition, which is accompanied by large volume change around T_C [13, 14]. Admixture of Co into the alloy composition resulted in the rise of T_C to ~290K accompanied by a drop of ΔS_M to ~ 13.5 J (kg K)$^{-1}$ at the alteration of magnetic field of 5T [15].

In the $LaFe_{11.8}Si_{1.2}$ alloy, the isothermal magnetization curves measured at various temperatures revealed hysteresis when increasing and decreasing external magnetic field [15]. As a consequence, characteristic shift of the maxima on the ΔS_M vs. T curves to higher temperatures with increasing $\mu_0 \Delta H$, is present. Such hysteresis is not observed for the alloys containing Co, where all maxima of ΔS_M (T) curves occur at around the Curie temperature [15]. Such behavior is frequently attributed to the change from first- to second order phase transition with the increase of the Co content. Apart from the hysteresis of the $M(T)$ curve, the XRD studies of the $LaFe_{11.8}Si_{1.2}$ alloy shown change of the lattice parameter at around the T_C of the $La(Fe,Si)_{13}$ phase [13, 14]. Therefore it was stated that the high entropy change is directly related to the first order phase transition. The aim of present work was to study the phase transition taking place around the Curie temperature for the Co containing alloys, where the phase transition occurs at around the room temperature. Especially, two types of studies were performed: (i) diffraction of monochromatic synchrotron radiation around Curie point and (ii) calculation of Landau coefficients from the magnetization curves measured at various temperatures [16]. The measurements were made for long time annealed arc-molten sample and short time annealed ribbons of the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy with 15 wt. % of La admixture. These results were compared with those obtained for the

$LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy bulk samples annealed at the same conditions, which was treated as a reference composition previously studied by Shen et al in [17].

2. Samples preparation and experimental methods

The ingot samples of both: the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy with various admixtures of La and the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy were obtained by argon arc-melting of the high purity elements. The rapidly solidified ribbons were melt-spun under the Ar atmosphere with the linear velocity of copper wheel surface of ~30 m/s. The samples were sealed into the quartz tubes under the Ar atmosphere and annealed at 1323K for 24h (in case of ribbon) and 49 days (in case of bulk specimens). The phase constitution was examined using a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation. The POWDERCELL 2.4 [18] and POWDERX [19] software packages were used for adjustment of the elementary cell lattice constant and simulation of theoretical diffraction patterns.

For the synchrotron experiment the ribbon samples were grinded in an agate mortar in order to make them more suitable for powder diffraction. Powder was put into thin-walled (0.02 mm) quartz capillary with outer diameter of 2 mm. The temperature of a specimen was controlled by a Peltier cooler with Pt100 temperature sensor. To ensure good thermal conductivity between the sample and the Peltier device a dedicated grease was used. XRD patterns were collected in a transmission mode in the temperature range between 243K and 303K with step of 5K. During each measurement, the sample was illuminated 5 times for 2 seconds by a well collimated 1x1 mm^2 photon beam having the wavelength λ=0.1234 Å. XRD patterns were recorded using a fast flat panel detector Perking Elmer 1621. Obtained two-dimensional XRD patterns were integrated in 2-

theta space using FIT2D program [20]. Sample to detector distance and detector orthogonality with respect to the incoming beam were determined by measuring the LaB_6 standard reference.

The magnetocaloric effect was studied using indirect methods based on the measurements of magnetization curves at various temperatures with using MPMS Quantum Design XL-5 system operating in the magnetic fields up to 5T. Order of phase transitions were investigated by Landau theory based on magnetic measurements and DSC studies, which were carried out using Perkin - Elmer DSC 8000 at temperature range from 180 to 360K with step 40K/min.

3. Results and discussion

In order to obtain the best magnetocaloric properties for the $La(Fe,Si)_{13}$-type alloys, formation of single phase during manufacturing route is crucial. Our preliminary studies have shown that using stoichometric composition for preparation of this alloy resulted in formation of relatively large fraction of α-Fe phase. This led us to a conclusion that the arc-melting process used for synthesis of the base alloy causes the evaporation of La [21,22]. This has an effect in formation of lower fraction of the $La(Fe,Co,Si)_{13}$ during annealing at 1323K for 49 days. Therefore we have decided to introduce the La surplus in order to improve the formation of this phase.

In Fig. 1 the XRD data for annealed samples of the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy with various admixtures of La from 0 to 30 wt. % are presented. It was shown that the La admixture does not eliminate the presence of α-Fe phase, however it can significantly decrease its fraction, especially for the composition with the 15 wt.% excess of La

admixture. Therefore, this alloy was selected for further studies of magnetocaloric effect. Similar behavior was observed by other authors. [23,24]

In Figs. 2 and 3 the detailed X-ray diffraction patterns measured at room temperature for annealed bulk samples of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ and the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy with the 15 wt. % excess of La are presented. The phase analysis revealed similar constitution of all alloy specimens. The majority (of ~95 vol. %) was attributed to the $La(Fe,Si)_{13}$ type phase of cubic $NaZn_{13}$–type structure (space group Fm3c) [7,8], while the rest corresponds to α-Fe. The calculation of the lattice parameter for the $La(Fe,Co,Si)_{13}$ phase revealed some differences between the investigated alloys. For the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$, the lattice constant reaches 11.55Å and decreases to 11.49Å for the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy. In case of ribbon samples calculation of lattice constant revealed an increase of this parameter to 11.56Å and 11.50Å for $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ and $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloys, respectively.

In order to examine the evolution of lattice parameter around the T_C, further studies were carried out on annealed bulk and ribbon samples of the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy with 15 wt. % excess of La. The measurements were performed at various temperatures ranging from 243K to 303K using synchrotron radiation. The diffraction patterns together with Miller indexes for the $La(Fe,Co,Si)_{13}$ phase measured for the ribbon sample at selected temperatures are shown in Fig. 4. Detailed inspection of XRD patterns revealed systematic shift of peak positions of the dominant $La(Fe,Co,Si)_{13}$ phase toward lower angles with the decrease of temperature. Such behavior indicates change of the lattice parameter of the $La(Fe,Co,Si)_{13}$ phase.

Regarding the fact that $a=d_{hkl}/(h^2 + k^2 + l^2)^{1/2}$, the Bragg equation can be rewritten in the form:

$$(h^2 + k^2 + l^2) = a\frac{2\sin(\theta)}{\lambda} \qquad (1).$$

Subsequently the lattice patameter *a* can be obtained from the slope of dependence introduced by equation 1.

The temperature dependence of the lattice parameter *a* is shown in Fig. 5. With decreasing temperature the lattice parameter *a* is increasing thus indicating expansion of the unit cell on cooling. This behavior is observed for both investigated specimens. The lattice parameter of the ribbon is greater than that for the bulk sample. Such phenomenon was observed for $LaFe_{11.57}Si_{1.43}$ in [25]. This behavior is not clearly explained until now. The possible reason for such change might be the presence of different internal stresses, that can be introduced during rapid cooling of the annealed samples, lower in case of bulk (due to lower heat exchange during cooling in water) and higher in case of ribbon. For temperatures lower than 253K the lattice constant of the $La(Fe,Co,Si)_{13}$ phase has changed slightly with a tendency to saturation at low temperatures. Above 253K the *a* parameter gradually decreased reaching the inflection point at ~283K. This characteristic behavior suggests that except the magnetic transition around the Curie point, additional structural change independent on the applied magnetic field, affect the exchange integral of the $La(Fe,Co,Si)_{13}$ phase. This eventually impacts the value of the magnetic entropy change in this temperature range. However, unlike in case of first order phase transition, a gradual decrease of the unit cell volume with increasing temperature around T_C may be related to the irregular substitution of the Fe positions by Co atoms.

For both investigated alloys the isothermal magnetization curves were measured in an external magnetic field up to 5T. From those curves the Arrott plots were constructed for all investigated alloys bulk and ribbons in order to determine both the

Curie temperature and analyze the magnetic phase transition around T_C. Arrott plots for all studied samples were presented in Fig. 6. As shown in [15], the slope of M^2 vs. H/M curves is directly related to the order of phase transition. In the case of materials where the magnetocaloric effect is governed by the first order phase transition, a non-monotonic and negative slope of Arrott plots around the T_C were observed. However for those where the second order transition occurs, a monotonic and positive slope Arrott plots around T_C were measured [26, 27]. For the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alike bulk and ribbon alloy with the 15 wt. % excess of La, the M^2 vs. H/M curve at T_C can suggest presence of second order phase transition. In case of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy, the Arrott plot at Curie temperature has positive slope and is almost straight line. It also suggests occurrence of second order phase transition. An alternative method for studying the phase transition around the Curie temperature is based on the Landau theory for itinerant electron metamagnetism [20]. In this approach the relation between magnetization M and magnetic field H derived from the free energy formula [28] is given by:

$$\mu_0 H = c_1(T)M + c_2(T)M^3 + c_3(T)M^5 \qquad (2)$$

Here $c_1(T)$, $c_2(T)$, $c_3(T)$ are the Landau coefficients.

The temperature dependences of the $c_1(T)$ and $c_2(T)$ are used to distinguish the first- from the second-order magnetic phase transitions [16, 29]. The $c_1(T)$ reaches minimum value in T_C, while $c_2(T)$ determines the order of phase transition. In Fig. 7 and 8 the temperature dependences of the Landau coefficient are shown for both alloys in bulk form. The c_1 coefficient in both cases has positive values reaching minimum at Curie point. The Landau coefficient c_2 changes from positive to negative value at the Curie point T_C for the materials revealing second order phase transition, while in case of the

first order transformation such change occurs at higher temperature T_0 than T_C [29]. It was shown that for the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy, T_C and T_0 take the same value (Fig. 7). A different result was obtained for the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy (Fig. 8), where T_0 is a bit higher than T_C determined from minimum of $c_1(T)$ curve. This anomaly may be related to the structural change in the $La(Fe,Co,Si)_{13}$ phase.

The magnetic entropy change for investigated alloys was determined from the magnetization curves measured at various temperatures around T_C using Maxwell relation [30] implemented to the Mathematica 7.0 software [31]:

$$\Delta S(T,H) = \int_0^H \left(\frac{\delta M(T,H)}{\delta T} \right)_T dH \qquad (3)$$

where: T – temperature; $M(T,H)$ – magnetization ; H – the magnetic field.

The ΔS_M vs. T curves determined for various changes of external magnetic fields ΔH are shown in Fig. 9 for all investigated alloys.

In case of the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy, the maximum entropy change $|\Delta S_M|$ for $\mu_0 \Delta H$=5T reaches ~14J/(kgK), and ~13J/(kgK), respectively for ribbon and bulk samples. However for the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy, $|\Delta S_M|$ values are two times smaller in bulk specimens and more than tree times lower in ribbons. That suggests significant impact of Al on the magnetic entropy change.

Calculated temperature dependences of Landau coefficients as well as diffraction of the monochromatic synchrotron radiation carried out at various temperatures indicate that the magnetic entropy change in the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy with 15 wt.% of La excess is related not only to the ferro- to paramagnetic phase transition but also to the change of

the lattice parameter independent on the magnetic field applied to the sample. However, constructed Arrott plots suggest the second order phase transition.

Although in [15] authors suggest the change from first to the second order phase transition in $LaFe_{11.8-x}Co_xSi_{1.2}$ (x=0, 0.4; 0.8) alloys based on the slope of Arrott plots, however in paper [17] Shen et al suggested the presence of the first order transition base on temperature dependences of magnetization and asymmetrical shapes of temperature dependences of ΔS_M in $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy. Similar asymmetry was observed for $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy with 15 wt. % of La excess (Fig. 9) alike for bulk and ribbon samples.

In case of Al containing alloy the $\Delta S_M(T)$ are symmetrical thus suggesting that the Al addition causes in the second order phase transition related to the weakening of the itinerant electron metamagnetic transition, thus leading to the decrease of the ΔS_M values [17].

DSC curves measured for bulk samples (x=0, 0.6) were shown in the fig. 10. In case of the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy sample with 15 wt. % excess of La, on DSC curves measured under both: heating and cooling conditions, a peak near Curie temperature of the $La(Fe,Co,Si)_{13}$ phase was observed. Maximum of this peak corresponds the temperature of 278K in case of heating conditions. Furthermore under cooling conditions the maximum of this peak was shifted to 264K. This behavior suggests occurrence of hysteresis, which is characteristic for first order phase transition. On the other hand, in DSC curves measured for the Al doped sample lambda peak was observed at T_C, typical for the second order phase transition [32].

Conclusions

In the present work the comparison of phase constitution and magnetic properties for $LaFe_{11.0}Co_{0.8}Si_{1.2}$ and $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloys are presented. In both cases long time heat treatment at 1323K for 49 days resulted in formation of almost single phase materials containing majority of $La(Fe,Co,Si)_{13}$ and small fraction of α-Fe. Admixture of 15 wt.% of La caused significant decrease of the α-Fe fraction in the phase constitution of the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy. The gradual decrease of lattice constant for the $La(Fe,Co,Si)_{13}$ phase with increasing temperature around T_C independent on the applied magnetic field indicates that a structural changes accompanying ferro- to paramagnetic transition are responsible for the high magnetic entropy change around T_C in the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy. This structural change may have the effect in the temperature dependences of Landau coefficients. Addition of Al into the alloy composition resulted in a switch to the typical second order phase transition. This has also caused the reduction of magnetic entropy change around T_C for the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy. DSC measurements carried out for sample of $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy with 15 wt. % excess of La under heating and cooling conditions, indicated occurrence of crystalline change. Additionally hysteresis of this behavior was observed, which is typical for first order phase transition. In case of the sample doped with Al, lambda peaks at heating and cooling conditions were observed, confirming second order phase transition at Curie temperature.

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Figure captions:

Fig. 1. The X-ray diffraction patterns measured for the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ with various admixtures of La annealed at 1323K for 49 days

Fig. 2. XRD scan and theoretical diffraction pattern for the bulk sample of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy annealed at 1323K for 49 days

Fig. 3. XRD scan and theoretical diffraction pattern for the bulk sample of the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy annealed at 1323K for 49 days

Fig. 4. Diffraction patterns measured at selected temperatures using monochromatic synchrotron radiation (λ=0.1234Å), for the ribbon sample of the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy with an excess of 15 wt. % of La

Fig. 5. Temperature dependence of the lattice parameter a of the $La(Fe,Co,Si)_{13}$ phase

Fig. 6. Arrott plots measured for the bulk sample of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy bulk a) and ribbon b) and $LaFe_{11.0}Co_{0.8}Si_{1.2}$ with 15 wt. % excess of La bulk c) and ribbon d)

Fig. 7. Temperature dependences of the Landau coefficients $c_1(T)$ (a), $c_2(T)$ (b) and $c_3(T)$ (c) for bulk specimen of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy

Fig. 8. Temperature dependences of the Landau coefficients $c_1(T)$ (a), $c_2(T)$ (b) and $c_3(T)$ (c) for bulk specimen of the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy with admixture of 15wt.% of La

Fig.9. Magnetic entropy change ΔS_M vs. temperature T measured for various changes of external magnetic fields $\mu_0 \Delta H$ on bulk specimens of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy (a) and ribbon (b), and for bulk specimen of the $LaFe_{11.0}Co_{0.8}Si_{1.2}$ alloy with excess of 15wt.% of La (c) and ribbon (d)

Fig. 10. DSC curves measured for bulk specimens of the $LaFe_{11.0}Co_{0.8}(Si_{1-x}Al_x)_{1.2}$ for x=0.6 a) and x=0 b), respectively.