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Structural and Magnetocaloric Study of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ Alloy

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In this study, we have investigated the microstructure and magnetic entropy change of annealed $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy in a form of bulk samples and melt-spun ribbons. The bulk samples were annealed at 1323 K for 20 and 49 days and the maximum values of the magnetic entropy change $|\Delta S_M|$ obtained after the change of external magnetic field from 0 to 5 T reached 7.5 J kg^{-1} K^{-1} and 7.7 J kg^{-1} K^{-1}, respectively. For the melt-spun ribbon annealed at the same temperature for 1 h, the maximum value of $|\Delta S_M|$ reaches 4.5 J kg^{-1} K^{-1}. The temperature corresponding to the maximum entropy change increased from 292 K for bulk samples to 295 K for melt-spun ribbons. The lower values of the magnetic entropy change in the melt-spun $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ are attributed to the presence of higher volume fraction of the secondary bcc-Fe phase in the ribbon samples.

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1. Introduction

Since the discovery of the giant magnetocaloric effect in $Gd_5Ge_2Si_2$ in 1997 by Pecharsky and Gschneidner [1], studies were focused on the search for less expensive materials that reveal comparable magnetocaloric characteristics. Interesting example is the $La(Fe,Si)_{13}$ compound with a cubic $NaZn_{13}$-type structure and space group $Fm3c$ [2, 3], that shows giant magnetocaloric effect near room temperature. The magnetic entropy change is observed in a wide range of temperatures depending on the alloy composition [4–7]. Large value of the $|\Delta S_M|$ is due to both: a second-order phase transition from ferro- to paramagnetic state in the $La(Fe,Si)_{13}$, and a first-order transformation that involves a change of the unit cell volume at the Curie point [8]. In alloys with $NaZn_{13}$-type cubic structure, the only stable ferromagnetic phase is $LaCo_{13}$, while both $LaFe_{13}$ and $LaNi_{13}$ phases are metastable [9]. It was shown in [10] that small admixture of Si or Al elements leads to stabilization of $LaFe_{13}$ phase. Furthermore, in order to increase the Curie point, an appropriate admixture of Co is used [11].

The aim of present work was to study the phase constitution and magnetocaloric effect in $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy processed in a form of bulk and ribbon samples.

2. Sample preparation and experimental methods

The ingot samples of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy were obtained by argon arc-melting of constituent elements of high purity. From the ingot samples, the ribbon was melt-spun under an Ar atmosphere with the linear wheel speed of ≈ 20 m/s. Both bulk and ribbon samples were sealed-off in quartz tubes under low pressure of argon and annealed at 1323 K. The annealing process was carried out for 1 h in case of ribbon sample while the bulk samples were annealed for 20 and 49 days. X-ray diffraction data were obtained at room temperature using Bruker D8 Advance diffractometer with Cu K_α radiation. The fitting of the experimental X-ray diffraction pattern was performed using PowderCell 2.4 [12] software, that allowed to adjust the units cell parameters of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ phase. The samples were subjected to the mechanical polishing and etching for 3 s in 0.5% nital solution in order to reveal microstructure using metallographic microscope NEOPHOT-32. Magnetic measurements were carried out using Magnetic Property Measuring System model MPMS-XL-5 (Quantum Design) equipped with 5 T superconducting magnet.

3. Results and discussion

Figure 1 shows the X-ray diffraction pattern obtained for the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy bulk samples annealed at 1323 K for 20 days. Positions of peaks corresponding to α-FeSi and indexed peaks attributed to the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ phase are also shown in this figure. For calculations of theoretical spectra corresponding to the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ phase, the space group symmetry $Fm3c$ was assumed. In the elementary cell of this phase, La atoms occupy 8a positions, while Fe atoms are placed statistically in 8b and 96i sites. It was assumed that Co, Si and Al can randomly substitute Fe atoms in 96i positions [13]. These assumptions allowed to adjust parameters of elementary cell of the

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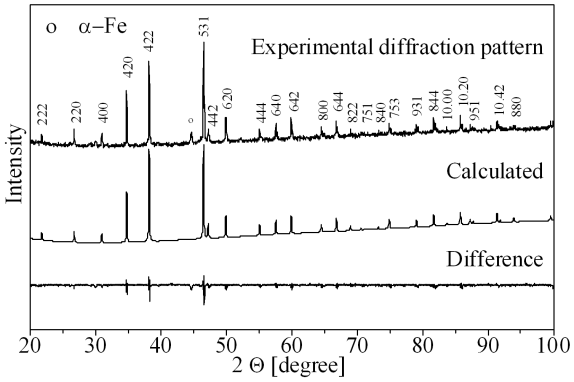

Fig. 1. Measured and calculated X-ray diffraction patterns of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy bulk sample annealed at 1323 K for 20 days.

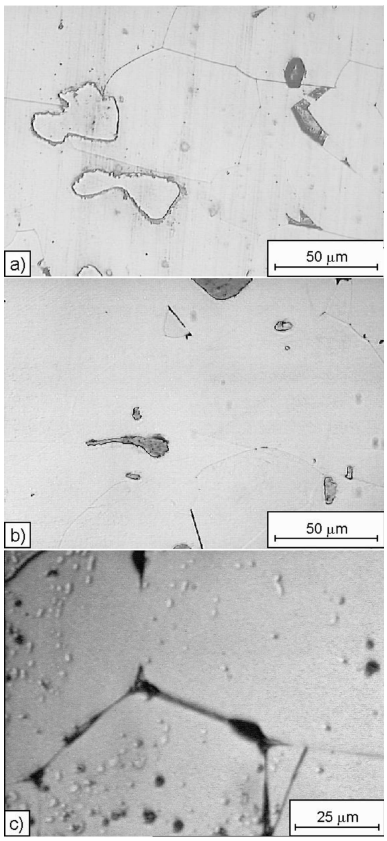

Fig. 2. Microstructure of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy bulk samples annealed at 1323 K for 20 days (a), 49 days (b), and for ribbon samples annealed at 1323 K for 1 h (c).

$LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ phase and to simulate theoretical X-ray diffraction. The differences between both spectra are also shown in the figure.

Microstructure of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy after annealing at 1323 K for 20 and 49 days, respectively for bulk samples and 1 h for ribbon sample are shown in Fig. 2.

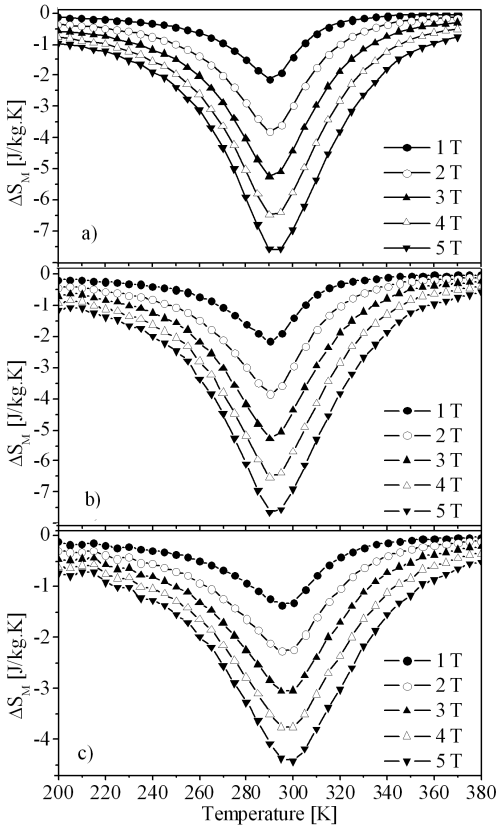

Fig. 3. The magnetic entropy changes $|\Delta S_M|$ vs. temperature T calculated for different changes of external magnetic field ΔH up to 5 T for the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ bulk sample annealed for 20 days (a), bulk sample annealed for 49 days (b), melt-spun ribbon annealed for 1 h (c).

The result of annealing of bulk samples at 1323 K for 20 and 49 days is uniform microstructure. In case of ribbons similar microstructure is obtained after annealing for only 1 h at 1323 K.

The magnetic entropy changes $|\Delta S_M|$ were calculated using the Maxwell thermodynamic relation [14]:

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

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

The dependences of $|\Delta S_M|$ vs. temperature, calculated for different changes of external magnetic field ΔH are shown in Fig. 3.

The figures show characteristic maxima of $|\Delta S_M|$ around the Curie point. For the change of external magnetic field ΔH of 5 T the magnetic entropy change $|\Delta S_M|$ reaches 7.5 J kg^{-1} K^{-1} and 7.7 J kg^{-1} K^{-1} at $T_C \approx 292$ K for the bulk samples annealed for 20 and 49 days, respectively. Calculated values for the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ bulk samples annealed at 1323 K for 49 days are comparable to those for the Al-free alloy having similar composition reported in [6]. The

maximum $|\Delta S_M|$ value of 4.5 J kg^{-1} K^{-1} at $\Delta H = 5$ T was obtained for the annealed melt-spun ribbon samples at 297 K. This value is lower than those reported for Al-free melt-spun samples reported in [15]. The observed lower magnetic entropy changes are attributed to the presence of higher volume fraction of the secondary bcc-Fe phase in our alloy.

4. Conclusions

The main drawback of the investigated alloy in the bulk form is long time annealing that leads to formation of desired phase with $NaZn_{13}$-type structure. Therefore application of melt-spinning process was used as an alternative way of processing of the samples, due to the expected time reduction needed for obtaining appropriate alloy constitution. It was shown that melt spinning method followed by short annealing results in an increase of the Curie temperature. On the other hand, the maximum value of the magnetic entropy change of $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ ribbon has decreased due to the presence of higher volume fraction of the secondary bcc-Fe phase but it remained still appreciable.

Acknowledgments

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