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The evolution of microstructure in annealed LaFeSi-type alloys

PIOTR GĘBARA[1*], PIOTR PAWLIK[1], EDYTA KULEJ[2], JERZY J. WYSŁOCKI[1], KATARZYNA PAWLIK[1], ANNA PRZYBYŁ[1]

[1]Institute of Physics, Faculty of Processing Materials, Technology and Applied Physics, Częstochowa University of Technology, Armii Krajowej 19, 42-200 Częstochowa, Poland

[2]Institute of Materials Engeenering, Faculty of Processing Materials, Technology and Applied Physics, Częstochowa University of Technology, Armii Krajowej 19, 42-200 Częstochowa, Poland

[*]Corresponding author: pgebara@wip.pcz.pl

The evolution of microstructure and the phase constitution of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy in as-cast state and after subsequent annealing at 1323 K for 10, 20, 49 days was studied. In the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy after arc-melting, the dominant dendritic α-Fe phase crystallizes, which is confirmed by X-ray diffraction. Annealing of the samples resulted in evolution of microstructure and the phase constitution. Prolonged annealing of the samples causes almost full homogenization of the alloy with the single-phase structure identified as $La(Fe_{0.85}Co_{0.06}Si_{0.04}Al_{0.05})_{13}$ phase of the $NaZn_{13}$-type structure.

Keywords: microstructure, magnetocaloric materials, X-ray diffraction.

1. Introduction

Since the discovery of the giant magnetocaloric effect (MCE) in $Gd_5Si_2Ge_2$, where the magnetic entropy change $|\Delta S_M|$ at $T_c = 276$ K reaches about 18.5 $\mathrm{J kg^{-1} K^{-1}}$ under the change of magnetic field ΔH to 5 T field [1], the intensive studies were focused on materials that revealed similar behavior near room temperature. Relatively low price and specific magnetic properties of La–Fe–Si type alloys were the main reasons for their investigation due to the possible application as active elements in magnetic refrigerators. The phase responsible for their unique properties is based on cubic $NaZn_{13}$-type structure (space group *Fm*3*c*) [2, 3]. However, the MCE is observed in a wide range of temperatures depending on the composition of alloy [4–7]. High value of $|\Delta S_M|$ is the result of two simultaneously occurring phase transformations: *i*) a second order magnetic transition from ferro- to paramagnetic state in the $La(FeSi)_{13}$ phase, and *ii*) a first order transition at about the Curie point. For various alloy compositions the giant magnetocaloric effect occurs, when the transition from ferro- to paramagnetic state coincides with the first order transformation of the phase responsible for this phenomenon [8]. In the case of the alloys investigated, the first order transition involves a change of the lattice parameter, which consequently leads to dramatic drop of the magnetic exchange coefficient [8, 9]. Therefore, the most important factor in processing the alloy is to generate sufficiently large volume fraction of the $La(FeSi)_{13}$ phase responsible for their unique properties. In Fe-based alloys the $LaFe_{13}$ phase is metastable in contrast to the stable $LaCo_{13}$ phase observed in Co-based alloys [10], therefore additions of Si and Al elements are used to stabilize this phase [11]. Furthermore, addition of Co is responsible for an increase in the Curie temperature of the $NaZn_{13}$-type phase [12]. The aim of the present work was to study the evolution of the microstructure and the phase constitution of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy in as-cast state and after subsequent annealing at 1323 K for 10, 20, 49 days.

2. Experiment

The $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ master alloy was prepared by arc-melting of high purity elementes in an Ar atmosphere. The ingot samples were subsequently sealed-off in a quartz tube under the low presure Ar atmosphere and annealed at 1323 K for 10, 20 and 49 days. The phase constitution of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy was investigated by means of X-ray powder diffractometry (XRD), using Seifert XRD 3003 diffractometer with Co$K\alpha$ radiation. The samples were subjected to the mechanical polishing in order to reveal microstructure using metalographic microscope NEOPHOT-32.

3. Results and discussion

In Figure 1, the XRD patterns for samples in as-cast state and after annealing at 1323 K for 10, 20 and 49 days are shown. The XRD analysis for the as-cast sample of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy has shown that the main crystalline phase consists of α-Fe grains. Subsequent heat treatment results in formation of $NaZn_{13}$-type phase. Long time anneling (for 49 days) resulted in changes of phase contribution of the samples, where dominant crystalline phase was the $La(Fe_{0.85}Co_{0.06}Si_{0.04}Al_{0.05})_{13}$ phase. Furthermore, the long time annealing shows a decrease of the α-Fe peaks in the diffraction pattern, which suggests a decrease of its volume fraction.

The mechanical polishing followed by etching of the samples for 3 s in 0.5% nital solution, were used to prepare the samples for microstructure observations. Microstructure of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy in as-cast state is shown in Fig. 2**a**.

The samples in as-cast state revealed dendrited microstructure, where dendrites were formed by α-Fe, while other alloy components were expelled into the dendrite arm spacing. The heat treatment at a temperature of 1323 K for 10 days resulted in radical change of microstructure (Fig. 2**b**), caused by formation of the $NaZn_{13}$-type phase. However, large amounts of inhomogenities are present. The XRD analysis suggests that in this stage, the sample consists mainly of the $NaZn_{13}$-type phase.

Similarly, the annealing for 20 days did not result in any significant change of their microstrucure (Fig. 2**c**). The annealing of the sample at 1323 K for 49 days caused homogenization of their microstructure, confirmed by XRD data, where only a minor volume fraction of remanent α-Fe phase was present (Fig. 2**d**).

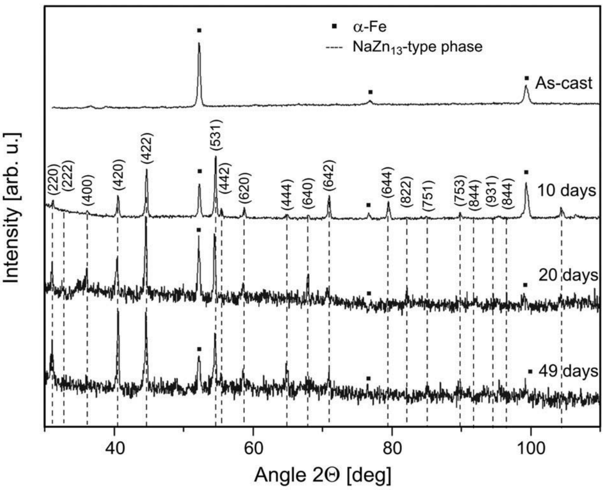

Fig. 1. X-ray diffraction patterns of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy samples: in as-cast state, after annealing at 1323 K for 10 days, after annealing at 1323 K for 20 days, and after annealing at 1323 K for 49 days.

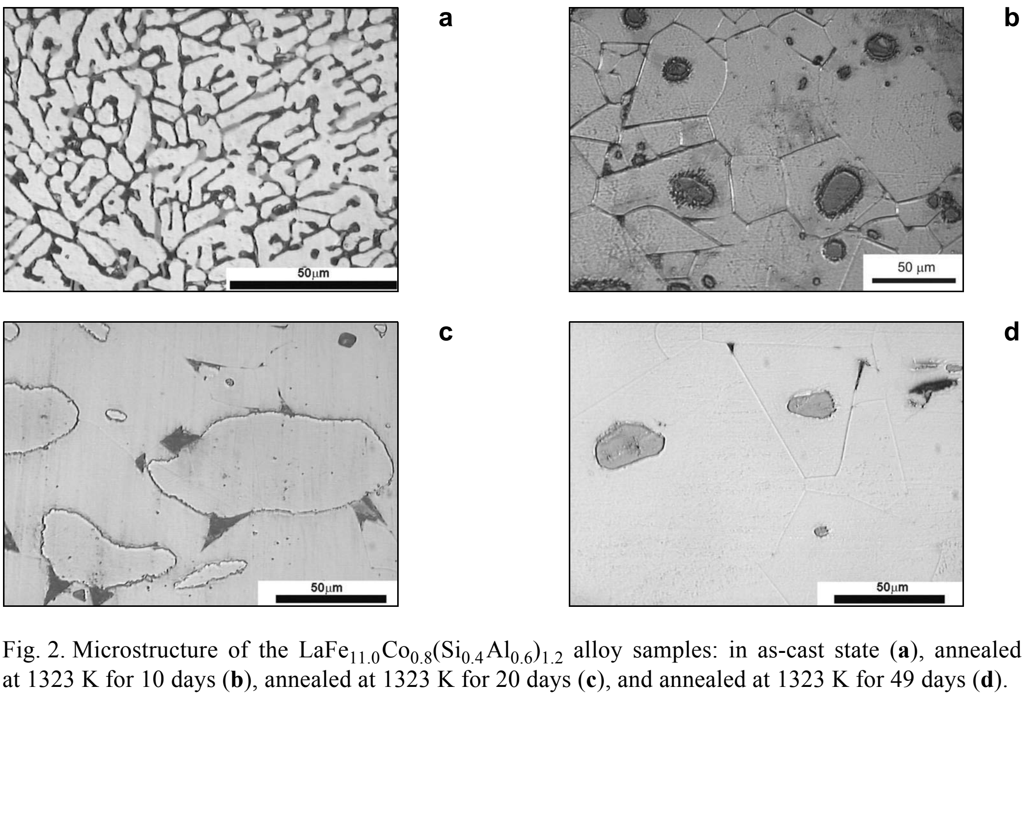

Fig. 2. Microstructure of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy samples: in as-cast state (**a**), annealed at 1323 K for 10 days (**b**), annealed at 1323 K for 20 days (**c**), and annealed at 1323 K for 49 days (**d**).

4. Conclusions

Based on the present investigation one can formulate the following conclusions:

– In the as-cast $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy, the dominant dendritic α-Fe phase crystallizes after arc-melting.

– Annealing of the samples resulted in evolution of the phase constitution and emerging $NaZn_{13}$-type structure, by solid state transformation.

– Long time annealing causes homogenization of the alloy where single-phase structure, identified as $La(Fe_{0.85}Co_{0.06}Si_{0.04}Al_{0.05})_{13}$ phase of the $NaZn_{13}$-type is formed.

References

[1] PECHARSKY V.K., GSCHNEIDNER K.A., *Tunable magnetic regenerator alloys with a giant magnetocaloric effect for magnetic refrigeration from ~20 to ~290 K*, Applied Physics Letters **70**(24), 1997, pp. 3299–3301.

[2] PALSTRA T.T.M., MYDOSH J.A., NIEUWENHUYS G.J., VAN DER KRAAN A.M., BUSCHOW K.H.J., *Study of the critical behavior of the magnetization and electrical resistivity in cubic La(Fe,Si)$_{13}$ compounds*, Journal of Magnetism and Magnetic Materials **36**(3), 1983, pp. 290–296.

[3] PALSTRA T.T.M., WERIJ H.G.C., NIEUWENHUYS G.J., MYDOSH J.A., DE BOER F.R., BUSCHOW K.H.J., *Metamagnetic transitions in cubic $La(Fe_x Al_{1-x})_{13}$ intermetallic compounds*, Journal of Physics F: Metal Physics **14**(8), 1984, pp. 1961–1966.

[4] FENG-XIA HU, BAO-GEN SHEN, JI-RONG SUN, ZHAO-HUA CHENG, GUANG-HUI RAO, XI-XIANG ZHANG, *Influence of negative lattice expansion and metamagnetic transition on magnetic entropy change in the compound $LaFe_{11.4}Si_{1.6}$*, Applied Physics Letters **78**(23), 2001, pp. 3675–3677.

[5] FENG-XIA HU, BAO-GEN SHEN, JI-RONG SUN, GUAN-JUN WANG, ZHAO-HUA CHENG, *Very large magnetic entropy change near room temperature in $LaFe_{11.2}Co_{0.7}Si_{1.1}$*, Applied Physics Letters **80**, 2002, p. 826.

[6] XU BO LIU, Z. ALTOUNIAN, *Effect of Co content on magnetic entropy change and structure of $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$*, Journal of Magnetism and Magnetic Materials **264**(2–3), 2003, pp. 209–213.

[7] JUN SHEN, YANG-XIAN LI, BO GAO, JI-RONG SUN, BAO-GEN SHEN, *Magnetic properties and magnetic entropy changes of $LaFe_{11.0}Co_{0.8}(Si_{1-x}Al_x)_{1.2}$ compounds*, Journal of Magnetism and Magnetic Materials **310**(2), 2007, pp. 2823–2825.

[8] FUJITA A., AKAMATSU Y., FUKAMICHI K., *Itinerant electron metamagnetic transition in $La(Fe_xSi_{1-x})_{13}$ intermetallic compounds*, Journal of Applied Physics **85**(8), 1999, pp. 4756–4758.

[9] TISHIN A.M., SPICHKIN Y.I., *The Magnetocaloric Effect and its Applications*, IOP Publishing Ltd., 2003.

[10] BUSHOW K.H.J., *Intermetallic compounds of rare-earth and 3d transition metals*, Reports on Progress in Physics **40**, 1977, pp. 1179–1256.

[11] KRYPIAKEWYTSCH P.I., ZARETSCHNIUK O.S., HLADYSCHEWSKYJ E.I., BODAK O.I., *Ternäre Verbindungen vom $NaZn_{13}$-Typ*, Zeitschrift für anorganische und allgemeine Chemie **358**(1–2), 1968, pp. 90–96.

[12] XU BO LIU, RYAN D.H., ALTOUNIAN Z., *The order of magnetic phase transition in $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ compounds*, Journal of Magnetism and Magnetic Materials **270**(3), 2004, pp. 305–311.

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