Journal of Magnetism and Magnetic Materials ■ (■■■■) ■■■–■■■

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Systematic study of the microstructure and magnetocaloric effect of bulk and melt-spun ribbons of La–Pr–Fe–Si compounds

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ARTICLE INFO

Article history:
Received 21 May 2013
Received in revised form
10 September 2013

Keywords:
$NaZn_{13}$-type La–Pr–Fe–Si compound
Microstructure
Magnetocaloric property
Bulk
Melt-spun ribbon

ABSTRACT

The microstructure evolution and the mechanism of the formation of $NaZn_{13}$-type 1:13 phase of $La_{0.6}Pr_{0.5}Fe_{11.4}Si_{1.6}$ alloys during annealing were investigated. After annealing at 1373 K for a proper period of time (15 days for the bulk alloy and 4 h for melt-spun ribbons), almost pure 1:13 phase was obtained. But with an overlong annealing time, 1:13 phase began to decompose and macroscopic α-Fe dendrites and La-rich phases appeared. Magnetocaloric effects of both $La_{0.6}Pr_{0.5}Fe_{11.4}Si_{1.6}$ bulk and melt-spun ribbons were also systematically studied. It was found that bulk sample exhibited larger thermal and magnetic hysteresis losses as a result of strong first-order transition, yet still showed higher magnetic entropy change and refrigerant capacity than those of melt-spun ribbons. By applying a field of 0–5 T, the magnetic entropy change and effective refrigerant capacity for bulk sample, respectively, were 25.2 J/(kg K) and 474.1 J/kg, while those of melt-spun ribbons turned out to be 21.9 J/(kg K) and 458.5 J/kg.

1. Introduction

Based on the magnetocaloric effect (MCE), numerous magnetic refrigerants have been intensively studied these years because of their potential application prospects, e.g., $Gd_5(Ge_{1-x}Si_x)_4$ [1], $MnFeP_{0.45}As_{0.55}$ [2], $La(Fe_{1-x}Si_x)_{13}$ [3], ε-$(Mn_{0.83}\ Fe_{0.17})_{3.25}Ge$ [4], and $Gd_{55}Co_{20}Al_{25}$ [5]. With prominent advantages in terms of giant magnetic entropy change $-\Delta S_M$, non-toxicity and low cost of raw materials, $LaFe_{13-x}Si_x$ compound is commonly accepted as one of the most promising magnetic refrigerants. The $LaFe_{13}$ phase does not exist because of its positive formation enthalpy; hence a third element Si/Al was introduced to stabilize a cubic $NaZn_{13}$-type structure. For $LaFe_{13-x}Si_x$, the phase transition is very sensitive to the Si content, i.e., it changes from first-order transition (usually accompanied by a typical itinerant electron meta-magnetic transition) to second-order transition corresponding to the Si content from $1.0 \le x \le 1.6$ to $1.6 < x \le 2.0$ respectively [6,7]. In addition, low Si content accompanies high entropy change and large hysteresis loss, which is the nature of first-order transition [8]. However, to achieve room-temperature refrigeration application, high efficiency, large entropy change, Curie temperature (T_C) near room temperature and low hysteresis loss are required [9]. Consequently, many efforts have been made to optimize magnetocaloric properties by partly substituting elements or interstitial atoms.

Liu et al. [10] reported the influence of different annealing temperatures on the microstructure and magnetic properties of $LaFe_{13-x}Si_x$ bulk with first-order transition. The conventional method to get the $LaFe_{13-x}Si_x$ phase is through long time heat treatment (more than 10 days), while Yan et al. [11] found that a melt-spun method could be applied to shorten the annealing time significantly to several hours. However, little work has been done about the contrast studies on the microstructure phase and MCE properties between the bulk alloys and the melt-spun ribbons. In our previous work [12], it was found that the $La_{0.6}Pr_{0.5}Fe_{11.4}Si_{1.6}$ compound had good magnetocaloric properties. Pr was introduced as the substitute element to increase the magnetic entropy change. Appropriate amount of La was added to suppress the appearance of α-Fe phase because usually it is difficult to obtain single $LaFe_{13-x}Si_x$ phase as a result of the interference of α-Fe phase. In this work, we systematically investigated the influence of preparation methods (bulk with arc melting followed by annealing and melt spun ribbons) and annealing time on the whole formation process of 1:13 phase, microstructure, magnetic and magnetocaloric properties for the optimized $La_{0.6}Pr_{0.5}Fe_{11.4}Si_{1.6}$ compounds.

2. Experiments

The ingots of $La_{0.6}Pr_{0.5}Fe_{11.4}Si_{1.6}$ were prepared by arc-melting in an argon atmosphere eight times, and the purities of the raw materials were 99% for La, 99% for Pr, 99.9% for Fe and 99.99% for Si. Part of the as-cast samples was annealed at 1373 K for 1–20

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http://dx.doi.org/10.1016/j.jmmm.2013.09.027

days in a vacuum quartz tube, and the other ingots were melt spun with a wheel speed of 25 m/s followed by annealing at 1373 K in a vacuum quartz tube for 1–8 h as well. After annealing, both the bulk and ribbons were quenched in ice water. The microstructure was observed by scanning electron microscopy (SEM) in back scattered electron (BSE) mode. The phase composition was measured by energy dispersive spectrometry (EDS), while phase identification was performed by using powder X-ray diffractions with CuKα radiation. The magnetic properties were measured by a physical property measurement system (PPMS). The magnetic entropy change was calculated from magnetization isotherms using the Maxwell relations

$$\Delta S_M(T,H) = S(T,H) - S(T,0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH.$$

3. Results and discussion

3.1. Microstructure

Through several times of arc-melting, a distributed structure could be obtained as shown in Fig. 1 (as-cast), in which white and black areas represent La-rich and α-Fe phases, respectively (detected by EDS). Fig. 1 clearly demonstrates the whole process of formation of 1:13 phase along with different annealing times at 1373 K. After being annealed for 1 day, La-rich and α-Fe phases diffused into each other and a third phase was pre-generated, as seen in Fig. 1 (1 day), and then 1:13 phase was preliminarily formed (Fig. 1 (7 days)). With increasing of annealing time to 10 days, 1:13 phase became the main phase. Interestingly, as the annealing time rose, the amount of 1:13 phase indicated an upward trend and reached almost 99% after 15 days annealing. However, with longer annealing time of 20 days, 1:13 phase seemed to begin to decompose, resulting in the separation of 1:13 phase to macroscopic α-Fe dendrites and La-rich particles instead, which is barely reported in previous papers. Because of the complicated formation mechanism, few reports mentioned the detailed process diagram and the exact origination of 1:13 phase. Liu et al. [10] proposed an intermediate phase, which is the so-called lamellae [13], between Fe-rich and 1:13 phases. To clarify the transformation, the sample after 1 day annealing was analyzed as well, as shown in Fig. 2. It could be seen in Fig. 2(a) that La-rich and α-Fe phases diffused into each other and a lamellar structure began to appear; at this time, 1:13 phase starts to form. From further magnification, as shown in Fig. 2(b), La-rich phase, Fe-rich phase, lamellae structure and 1:13 phase existed together, which were indexed as A, B, C, and D respectively (detected by EDS). That is to say, the lamellar structure is the precursor of 1:13 phase and this could be strongly proved by Fig. 2.

Compared to bulk alloys, the annealing time for melt-spun ribbons could be substantially shortened to several hours. Similarly, to describe the formation of 1:13 phase, different annealing times for melt spun ribbons ranging from 1 h to 8 h were set and the phase evolutions are shown by XRD in Fig. 3. According to Fig. 3, XRD patterns show that α-Fe phase was suppressed

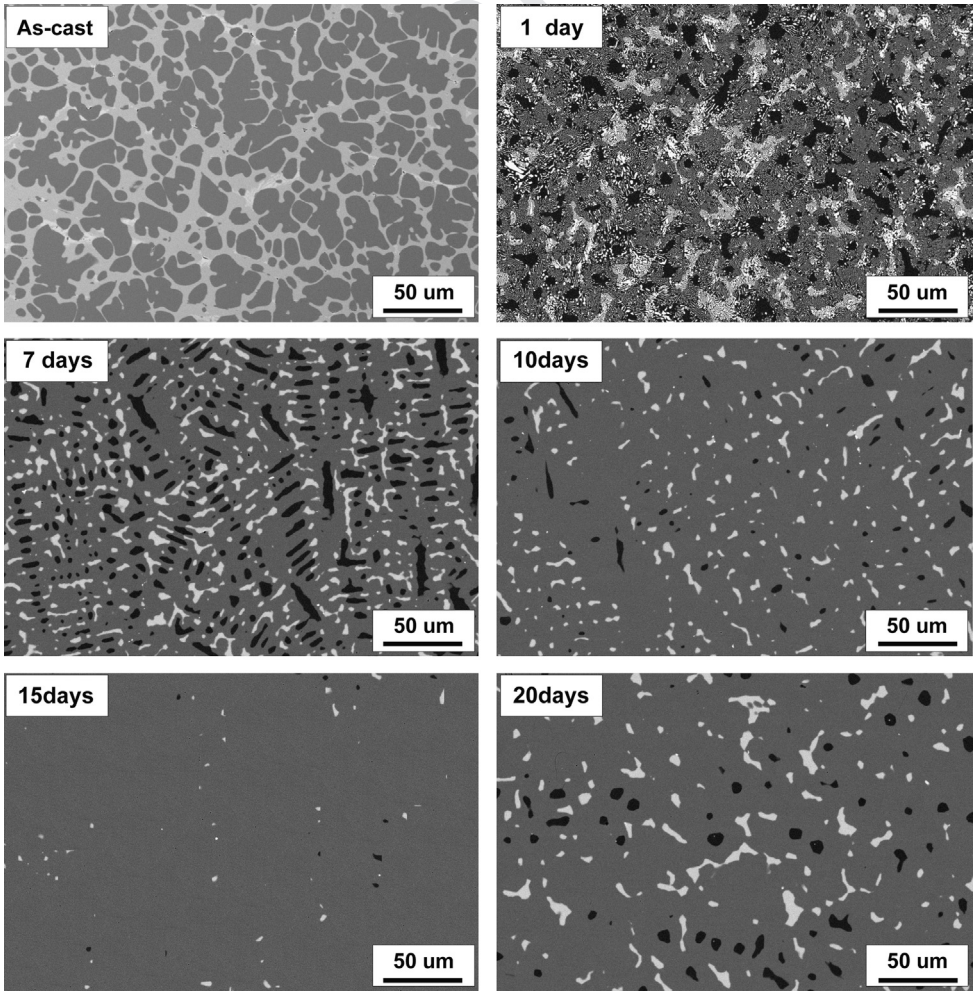

Fig. 1. Backscattered SEM images of $La_{0.6}Pr_{0.5}Fe_{11.4}Si_{1.6}$ bulk alloys annealed at 1373 K for different times.

Please cite this article as: J.J. Liu, et al., Journal of Magnetism and Magnetic Materials (2013), http://dx.doi.org/10.1016/j.jmmm.2013.09.027