Rare Metal Materials and Engineering
Volume 45, Issue 11, November 2016
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2016, 45(11): 2814-2817.

ARTICLE

Phase Formation and Magnetocaloric Effect in $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ Compounds Prepared by Ball-milling

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Abstract: The samples of $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06) were prepared by ball-milling with elemental powder and LaSi cast master alloys. After sintering at 1423 K for 30 min followed by quenching in water, an almost $NaZn_{13}$ type single phase was obtained. The study of magnetic properties reveals that the Curie temperature increases with Co content from x=0 to x=0.06 whereas the magnetic entropy change decreases. The alloy of $LaFe_{11.2}Si_{1.8}$ has a maximum magnetic entropy change ΔS_m of 6.5 J/(kg·K) near its Curie temperature under a magnetic field of 0~1.5 T, while the maximum magnetic entropy change is about 2.1 J/(kg·K) with x=0.06. Furthermore, the magnetization of ball-milled samples exhibits a second-order magnetic transition, which is interesting for magnetocaloric applications.

Key words: magnetocaloric effect; $La(Fe, Co, Si)_{13}$ compound; $NaZn_{13}$-type; ball-milling

Compared to conventional vapor compression systems, room temperature magnetic refrigeration based on the magnetocaloric effect (MCE) presents many advantages, such as high refrigeration efficiency, low noise, reliability and environment-friendly [1-3]. The MCE is related to an adiabatic temperature change as well as an isothermal magnetic entropy change of a magnetic material upon application of a magnetic field. To achieve the magnetic refrigerants working at room temperature, the magnetic refrigerant with a wide range of temperatures covering room temperature and giant magnetocaloric effect (GMCE) is one of the important factors. $LaFe_{13-x}Si_x$ alloys with cubic $NaZn_{13}$ type structure are commonly accepted as one of the most promising magnetic refrigerants. $LaFe_{13-x}Si_x$ compounds have some advantages, such as GMCE with lower price of raw materials and excluding deleterious elements. However, these alloys have two disadvantages in practical application. Firstly, the Curie temperature (T_C) is around 200 K of $La(Fe, Si)_{13}$ alloys[4], so they cannot directly be applied to room temperature magnetic refrigeration. They need to adjust T_C to room temperature while retaining their large magnetic entropy change. Secondly, the $NaZn_{13}$-type structure is hard to obtain directly from common solidification process due to the intrinsic incompleteness of a peritectic reaction: γ-Fe+L→$La(Fe,Si)_{13}(\tau_{1a})$, which often results in the mixed phases of α-Fe+$La(Fe, Si)_{13}(\tau_{1a})$+$La(Fe, Si)_{13}(\tau_4)$ [5]. Thus, the traditional preparing method obviously wastes a large amount of energy and time, and restricts the application of these materials in magnetic refrigeration. Recently several researches on the synthesis of $LaFe_{13-x}Si_x$ alloys by melt-spinning have been reported [4-9]. Shorter heat treatment is required for melt-spinning alloys compared to bulk alloys. It is the aim of this paper to examine the influence of ball-milling on the magnetic properties and the annealing time of $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06) alloys. The phase relation, Curie temperature and magnetocaloric effects of $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ compounds are investigated.

1 Experiment

The $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06) compounds were synthesized by ball-milling. LaSi alloy melt congruently at 1898 K according to Ref. [10] as precursor to prevent

Received date: November 11, 2015
Foundation item: National Natural Science Foundation of China (51161017); Scientific Research Foundation for Advanced Talents Inner Mongolia University (135145)
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oxidation of lanthanum was prepared by arc-melting under purified argon atmosphere. The LaSi ingot was ground to powder in an agate mortar. All powders including LaSi, Si and Fe were mixed in an agate mortar, and then loaded into a stainless steel vial under high-purity Ar atmosphere inside a glove box. The purities of the raw materials were larger than 99.5 wt%. Before sealing the vial, stainless steel balls were added. The powder to ball mass ratio was 1:4. The ball-milling was performed in a planetary mill (Fritsch Pulverisette-6). The as-milled powders were compacted and sealed under argon in a silica tube and annealed at 1423 K for 30 min followed by quenching in water. The phase purity and crystal structures were determined by powder X-ray diffraction (XRD) using Cu Kα radiation (λ=0.154 184 nm). Magnetic measurements were performed using a vibrating-sample magnetometer (Lakeshore 7410).

2 Results and Discussion

Fig.1 shows the X-ray diffraction (XRD) pattern of LaSi alloy at room-temperature. Besides the main phase LaSi, a small amount of $LaSi_2$ is observed in the as-cast LaSi compound. The phase composition and structural characterization of $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ compounds from XRD are listed in Table 1. The high energy ball-milling brings about the formation of an amorphous phase in which a large amount of α-(Fe, Si) (Fig.2) appear. A short annealing treatment of 30 min at 1423 K is enough to reduce the α-(Fe, Si) content as impurity phase and obtain a well phase with cubic $NaZn_{13}$ type structure in all $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ alloys. According to the XRD data refinement, the main diffraction peaks of the cubic $NaZn_{13}$-type structure phase obviously shifts to high angle with increasing the content of Co from x=0 to x=0.06. This is a sign of lattice contraction. It attributes to the radius of Co (0.167 nm) being smaller than that of Fe (0.172 nm)[11]. The lattice parameter gradually decreases from 1.1392 nm to 1.1388 nm with increasing Co content from x=0 to 0.06.

Fig.3 displays the magnetization isotherms of $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06) compounds measured under a magnetic field of 0.05 T during the heating process. All the measurements were performed on the annealed samples. The

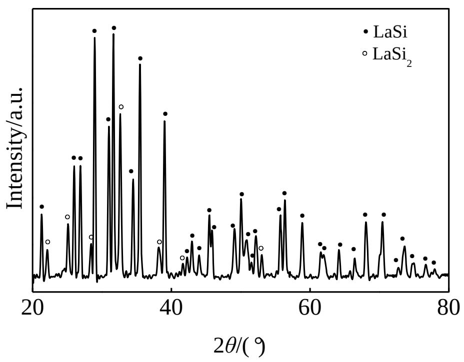

Fig.1 XRD pattern of LaSi alloy

Table 1 Structural characterization of $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06) from XRD

x	Phases	Lattice constant, a/nm
0	$NaZn_{13}$, α-(Fe,Si)	1.1392
0.02	$NaZn_{13}$, La_2O_3, α-(Fe,Si)	1.1391
0.04	$NaZn_{13}$, α-(Fe,Si)	1.1389
0.06	$NaZn_{13}$, La_2O_3	1.1388

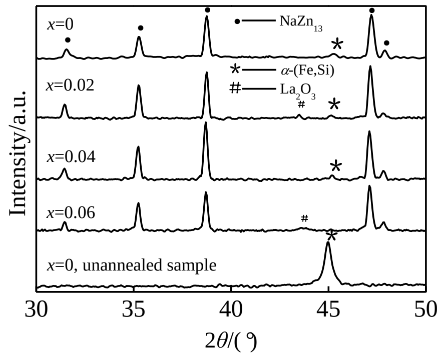

Fig.2 XRD patterns of $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06) annealed and unannealed

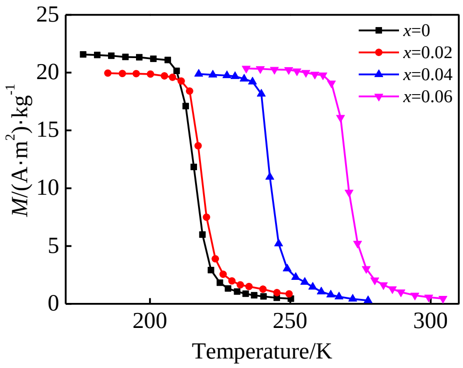

Fig.3 Temperature dependence of magnetization for $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06) measured under a field of 0.05 T

transition temperature is determined as the maximum of dM/dt in heating process. The Curie temperature is determined to be 214.5, 217.5, 243.5, and 269.5 K for samples x=0, 0.02, 0.04, 0.06, respectively. The T_C of $LaFe_{11.2}Si_{1.8}$ alloys is 214.5 K in our work, which is in accord with Ref. [11]. As previous reports[12], the increase of Curie temperature attributes to the strong Co-Fe exchange interaction in Co-substituted $La(Fe,Si)_{13}$ alloys. We note the Curie temperature of the $LaCo_{13}$ ferromagnetic alloy, T_C= 1297 K[13], is much higher than that of $La(Fe,Si)_{13}$ alloys. It indicates that Co-Co interactions are much stronger than those of the Fe-Fe in $NaZn_{13}$ alloys. Thus the increase of the Curie temperature in the Co-substituted alloys of $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ should mainly attribute to the Fe-Co and Co-Co interactions.

Fig.4 displays the magnetization isotherms as a function of magnetic field of the $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06) compounds for various temperatures in the field increasing

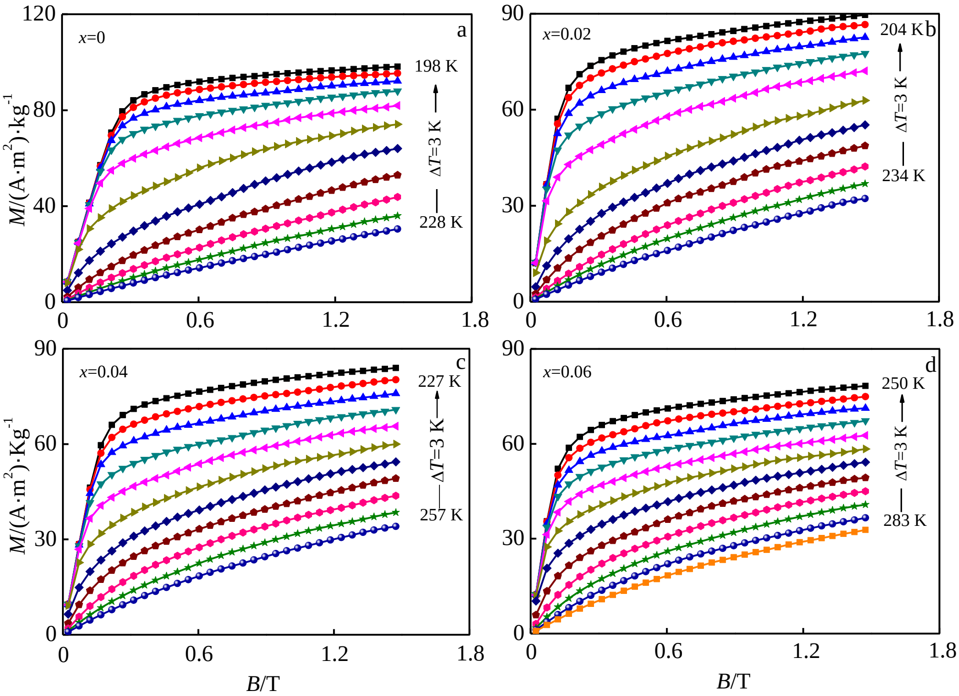

Fig.4 Magnetization isotherms of $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06) measured in the vicinity of T_C: (a) x=0, (b) x=0.02, (c) x=0.04, and (d) x=0.06

process from 0 to 1.5 T. The measurements were performed over a wide range of temperature with a temperature step of 3 K in the vicinity of the Curie temperature. It is found that the magnetization of the $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ compounds does not exhibit a clear metamagnetic behavior above T_C.

Fig.5 shows the compared Arrott plots for the $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ compounds. On the basis of I-S model, negative slopes in Arrott plots usually show a first-order transition and the linear relation in Arrott plot above the Curie temperature shows that a second-order transition occurs [14]. One can find that the Arrott plots above T_C for two samples display an almost linear relation, which is typical for a second-order magnetic transition from ferromagnetic to paramagnetic at T_C.

Magnetic entropy change $\Delta S_m(T, H)$ is derived by Maxwell relation from the isothermal magnetization data. Fig.6 shows the ΔS_m as functions of temperature and magnetic field for

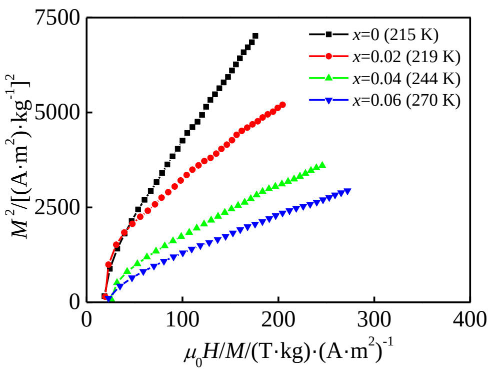

Fig.5 Arrott plots of $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06)

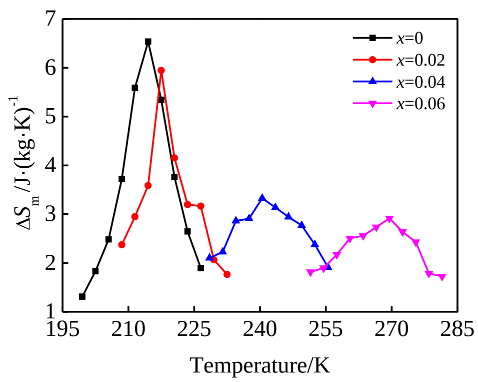

Fig.6 Magnetic entropy change ΔS_m as functions of temperature for $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$($x$=0, 0.02, 0.04, 0.06) compounds under a magnetic field change of 0~1.5 T

the $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06) compounds. It is found that the maximum magnetic entropy change of $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ compounds gradually decreases with increasing the Co content. The maximum magnetic entropy change of $LaFe_{11.2}Si_{1.8}$ is 6.5 J/(kg·K) in agreement with previous works [11] near its Curie temperature under a magnetic field of 0~1.5 T, while the maximum magnetic entropy change of $La(Fe_{0.94}Co_{0.06})_{11.2}Si_{1.8}$ is only about 2.1 J/(kg·K). This means that ball-milled $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ compounds have the same magnetocaloric behavior as bulk ones. According to the literature, the order of the magnetic transition changes from a strong first order to a weak first order and finally to a second order in annealed arc-melted $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$

compounds with increasing Co content[15]. The change in the order of the magnetic transition at its Curie temperature is responsible for the large decrease of ΔS_m in $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ compounds.

3 Conclusions

1) Applying the ball-milling technique of reactive sintering, the magnetocaloric bulk materials based on $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06) with tunable T_C are successfully produced. The compounds with cubic $NaZn_{13}$ type structure are obtained after 30 min heat treatment at 1423 K. This means a kind of saving in time and energy which is very significant for industrial application.

2) The lattice constant decreases and the T_C increases with increasing the Co content from x=0 to x=0.06. The magnetization of ball-milled samples exhibits a second-order magnetic transition from ferromagnetic to paramagnetic at T_C.

3) The very small magnetic hysteresis upon a field cycle reveals a good reversibility of magnetic entropy change on the applied field, which is considered to be a favorable characteristic for magnetic refrigeration applications.

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球磨制备的 $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ 化合物的相形成和磁热效应

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摘　要：将 LaSi 母合金和元素粉末混合，利用球磨工艺制备了 $La(Fe_{1-x}Co_x)_{11.2}Si_{1.8}$ (x=0, 0.02, 0.04, 0.06)样品。在 1423 K 的温度下烧结 30 min，然后放入水中快速冷却，就可以获得几乎为 $NaZn_{13}$ 型结构的单相化合物。磁性质的研究表明，样品的居里温度随着 Co 含量从 x=0 到 x=0.06 而提高，但是磁熵变减小。在 0~1.5 T 的外加磁场下，$LaFe_{11.2}Si_{1.8}$ 合金在其居里温度附近的最大磁熵变达到的 6.5 J/kg，而 x=0.06 的样品的最大磁熵变约为 2.1 J/(kg·K)。另外，球磨制备的样品还呈现了二级磁相变的特点，这对于磁热效应的应用非常有意义。

关键词：磁热效应；$La(Fe, Co, Si)_{13}$ 化合物；$NaZn_{13}$ 型；球磨

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