The study on the microstructure and the magnetocaloric effects in $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound at different annealing times

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Microstructure and magnetocaloric effects in $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound produced by induction furnace were investigated. $NaZn_{13}$-type structure (1:13) formed in $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound after being annealed at 1373 K for only 6 h. As annealing time increases, the grains grow up irregularly. A nearly single 1:13 phase is obtained after being annealed for 2 days. Annealing time is significantly reduced compared with that in conventional bulk $LaFe_{13-x}Si_x$ compounds. The short annealing time is of great advantage to application. The maximum magnetic entropy change of this compound is −4.9 J/K Kg under a magnetic field of 2 T and relative cooling power is 172.2 J/Kg.
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I. INTRODUCTION

$LaFe_{13-x}Si_x$ compounds with cubic $NaZn_{13}$-type structure have been studied in detail due to large magnetocaloric effect (MCE) and cheap raw materials.[1–3] Previous studies show that the compounds with $x \leq 1.6$ exhibit large MCE because of itinerant-electron metamagnetic transition, but the Curie temperature T_C is far below the room temperature.[4] However, the Curie temperature of $La(Fe_xSi_{1-x})_{13}$ compounds can be increased from 195 to 323 K by hydrogen absorption.[5,6] The large MCEs are obtained around room temperature by adjusting y in $LaFe_{13-x}Si_xH_y$ compounds. In addition, Curie temperature is tunable from 243 to 301 K with cobalt doping from $x=0.04$ to 0.08 in $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ compounds.[7] Carbon element as interstitial atom also can increase T_C.[8,9] In the cases of increasing Curie temperature above, magnetic entropy change decreases drastically with the addition of cobalt and carbon, while ΔS decreases slightly and adiabatic temperature change increases by hydrogen absorption. Besides, the hydrides are usually chemically unstable above a certain temperature. Recently, it is reported that $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}C_y$ compounds show large MCE near room temperature.[10]

On the other hand, 1:13 phase in $LaFe_{13-x}Si_x$ compounds is hard to be obtained directly from general casting process. It is formed from a peritectic reaction by annealing as-cast samples for a long time. Based on reported researches[1,2,4–10] on $La(Fe,Co)_{13-x}Si_x$ compounds, several weeks or 2 months are necessary to form single 1:13 phase in the compounds. Therefore, understanding of 1:13 phase formation in $La(Fe,Co)_{13-x}Si_x$ compounds is very important from an application viewpoint. A melt spinning processes is effective for 1:13 phase formation and shorten annealing time. Large undercooling of melts obtained by melt spinning method can suppress the nucleation of α-Fe (Co, Si) and enhances the formation of the 1:13 phase.[11,12] However melt spun $LaFe_{13-x}Si_x$ ribbons could not meet the size requirement (at least 0.2 mm) of magnetic refrigeration material, which is applied in the magnetic refrigeration machine.[13]

In order to find an applicable magnetic refrigeration material, 1:13 phase formation at different annealing times and magnetic entropy change of kilogram-level $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compounds were investigated in this paper.

II. EXPERIMENTAL PROCEDURE

Rod samples of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compounds with a diameter of 18 mm were prepared by induction furnace. The samples were sealed in a quartz tube and annealed at 1373 K for 6 h, 1 day, and 2 days, respectively. The crystal structures were identified by x-ray diffraction with Cu Kα radiation. The magnetic properties were measured using a vibrating sample magnetometer (LakeShore-7410). The microstructures were investigated by optical microscope and scanning electron microscope (SEM).

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction patterns of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compounds at room temperature at different annealing times. The results clearly indicate that the matrix phase of all specimens is 1:13 phase. Additionally, small diffraction peak of α-Fe phase is detected after annealing for 6 h.

Figure 2 shows backscattered SEM micrographs of as-cast sample. It is observed that two phases are present in the microstructure of as-cast sample. The energy dispersive spectroscopy results indicate that the darker portion is α-Fe phase and white phase is rich in La (>30 wt %), 1:13 phase with $NaZn_{13}$ structure is not found in the microstructure. Figure 3 shows backscattered SEM micrographs of the

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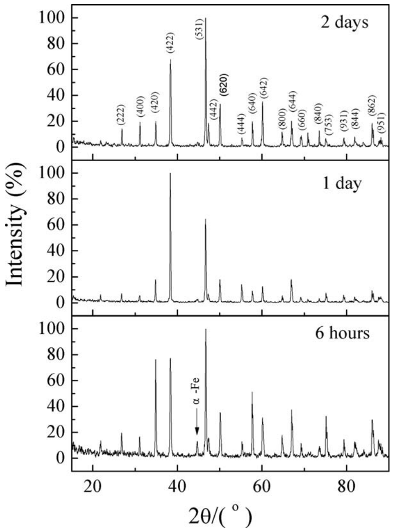

FIG. 1. X-ray diffraction patterns of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compounds (annealing for 3 h, 6 h, 1 day, and 2 days).

samples after annealed for 6 h, 1 day, and 2 days, respectively. When the sample of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound is annealed at 1373 K for 6 h, 1:13 phase has been already formed as the matrix phase. The darker portion in the matrix is α-Fe phase, while the white portion located in the grain boundary is La-rich phase. After being annealed for 1 day, α-Fe phase and La-rich phase decrease because peritectic reaction occurs between the two phases.

Additionally, some large grains are surrounded by other small grains during annealing processes. It indicates that the grains of 1:13 phase grow up irregularly and it may lead to the weakness of the mechanical properties of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound. When the compounds are annealed for 2 days, the grains further grow up. Although α-Fe phase and La-rich phase are still present, the amount of them is very small. The amount of α-Fe phase and grain size of 1:13 phase is evaluated from micrographs by quantitative metallography. It is found that when annealing time increases from 6 h to 2 days, the average grain size of 1:13 phase grows up and α-Fe phase volume decreases. When the compound is annealed for 6 h the average grain size of 1:13 phase has already been about 26 μm, while the α-Fe phase volume fraction is only 5.8%. It is apparent that the peritectic transformation is very fast in $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound. When $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound is annealed for 2 days, the average grain size of 1:13 phase is about 39 μm and the compound is almost single 1:13 phase. However, the general $LaFe_{13-x}Si_x$ bulk material should go

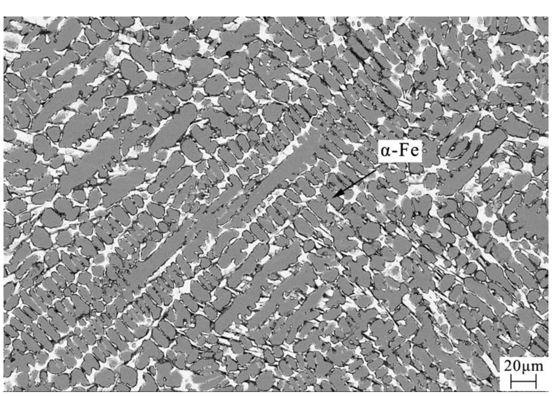

FIG. 2. Backscattered SEM micrographs of as-cast sample.

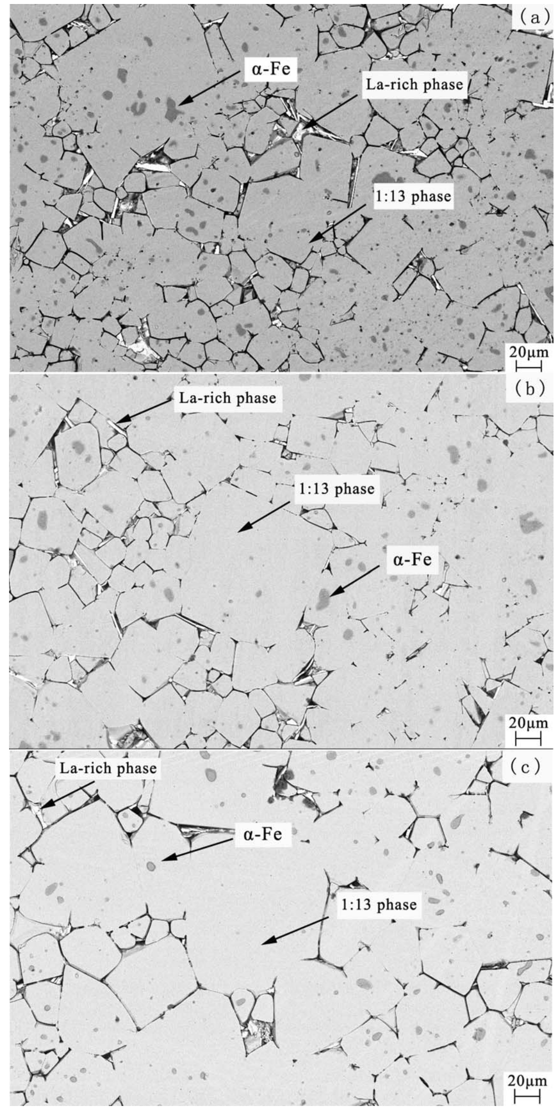

FIG. 3. Backscattered SEM micrographs of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound after being annealed at 1373 K at different times (a) 6 h, (b) 1 day, and (c) 2 days.

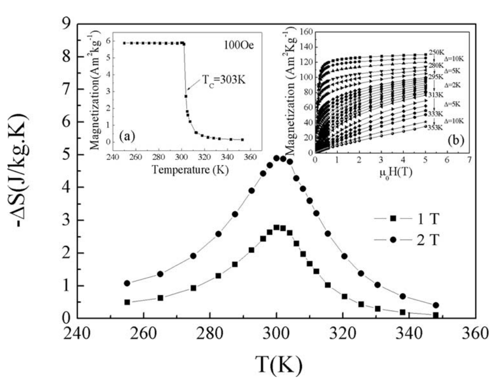

FIG. 4. Magnetic entropy changes of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound annealed for 2 days. (a) MT curve of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound. (b) Isothermal magnetization of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound.

TABLE I. The RCP, T_C, and $-\Delta S_M$ of some magnetic refrigeration materials.

Materials	RCP (J/Kg)	T_C (K)	$-\Delta S_M$ (J/Kg K) (2T)
Gd[a]	169	295	4.5
$MnFeP_{0.45}As_{0.55}$ [a]	145	304	14.5
$La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$ [b]	159	323	19.0
$La(Fe_{0.919}Co_{0.081})_{11.7}Al_{1.3}$ [c]	169	311	3.6
$LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$	172	302	4.9

[a]Reference 14.
[b]Reference 5.
[c]Reference 15.

through a few weeks or months to complete the peritectic transformation, in order to obtain single 1:13 phase. The short annealing time could be attributed to high content of both Si and Co in the $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound because the mixing heat of La–Si and La–Co is negative. Obviously, short heat treatment time is of great advantage to application.

The magnetic properties of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound annealed for 2 days are also studied. T_C of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound annealed for 2 days was determined by thermomagnetic curve (MT), shown as inset (a) in Fig. 4. Isothermal magnetization curves of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound on the heating are shown as inset (b) in Fig. 4. The curves show typical second order magnetic phase transition behavior. The magnetic entropy changes $-\Delta S_M$ as a function of temperature and magnetic field for $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound was calculated from isothermal magnetization curves using the Maxwell relation,

$$\Delta S_M = \int_0^H \left(\frac{\partial M(H,T)}{\partial T}\right)_H dH. \qquad (1)$$

The magnetic entropy changes of $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound under a magnetic field change of 0–2 T are shown in Fig. 4. Under a magnetic field of 2 T, maximum magnetic entropy change for $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound is about −4.9 J/Kg K. Relative cooling power (RCP) is also calculated from the magnetic entropy changes curves and it is about 172.2 J/Kg, seen in Table I. Table I also lists ΔS_M and RCP of other representative magnetic refrigeration materials calculated from Refs. 14, 5, and 15. Large RCP values for $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound indicate that this compound can be exploited for room temperature refrigeration material.

IV. CONCLUSIONS

1:13 phase with $NaZn_{13}$ structure was obtained in $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound after being annealed at 1373 K for 6 h. With annealing time increasing, the grains grow up irregularly and α-Fe phase volume decreases. An almost single 1:13 phase is obtained after being annealed for only 2 days. In addition, the maximum magnetic entropy change of this compound is −4.9 J/K Kg under a magnetic field change of 0–2 T and RCP is 172.2 J/Kg, which is larger than other representative magnetic refrigeration materials. So $LaFe_{10.8}Co_{0.7}Si_{1.5}C_{0.2}$ compound can be exploited for room temperature refrigeration material.

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