Magnetic and magnetocaloric properties in La–(Fe–Co)–Si

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Abstract

In this paper we present the results of study on the magnetic and magnetocaloric properties of LaFe\textsubscript{11-x}Co\textsubscript{x}Si\textsubscript{2} (x = 0, 1, 2, 3 and 4) ribbons prepared by using melt-spinning method. The results show that the glass forming ability (GFA) of the alloy is considerably influenced by the addition of Co. With increasing Co-concentration of the alloy, Curie temperature (T\textsubscript{C}) increases from ∼220 K (for x = 0) to ∼500 K (for x = 4). The maximum magnetic entropy change |\Delta S\textsubscript{M}|\textsubscript{max} of the alloy, which is achieved near T\textsubscript{C}, is larger than 1.2 J kg\textsuperscript{-1} K\textsuperscript{-1} (under magnetic change \Delta H = 12 kOe) for all the concentrations of Co. This has a significant meaning for magnetic refrigeration applications.

Keywords: Magnetocaloric effect, Curie temperature, rapidly quenched alloys

Classification number: 5.02

1. Introduction

Since its discovery, magnetocaloric effect (MCE) of material has been attracting many scientists because of the possibility of using it for magnetic refrigeration. The application of magnetocaloric materials in chillers has the advantages of not causing environmental pollution (unlike chillers using compression gases), capability of improving the cooling efficiency (saving energy), compact design, less noise and ability to be used in some special applications. Magnetic refrigeration is based on the principle of magnetic entropy change of the material. To have large magnetic cooling efficient, the MCE of the material should be large. There are three main factors to estimate potential magnetocaloric materials: the magnetic entropy change (\Delta S\textsubscript{M}), the adiabatic temperature change (\Delta T\textsubscript{ad}) and refrigerant capacity (RC). An ideal magnetic refrigerant has to possess large values of both the \Delta S\textsubscript{M} and RC around room temperature in low magnetic field.

Magnetocaloric materials are actually of interest to research nowadays due to new discoveries of both the mechanism and magnitude of MCE. The search for magnetocaloric materials with the possibility for applications in magnetic refrigeration at room temperature region are of more and more interest for scientific research. These materials include As-containing alloys (MnAsSb, MnFePAs, etc), La-containing alloys (LaFeSi), Heusler alloys (CoMnSi, NiMnSn, NiMnGa, etc), and ferromagnetic perovskite maganites [1–10]. Among these materials, amorphous magnetic or nanocrystalline materials are potential candidates [11–19] because they (i) undergo second-order magnetic phase transitions which present a broad \Delta S\textsubscript{M} peak around the Curie temperature T\textsubscript{C}, (ii) possess large RC, (iii) do not exhibit structural changes [15] and (iv) have small magnetic and thermal hysteresis, high electrical resistivity and good mechanical properties [16]. Among this kind of materials, rare-earth-based amorphous alloys have high \Delta S\textsubscript{M} peak and large RC. Particularly, LaFe\textsubscript{13}-based

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alloys have attracted intensive attention due to their low price, giant magnetocaloric effect (GMCE) and high thermal conductivity. But their Curie temperature $T_C$ is under room temperature, making them unsuitable for ambient-temperature applications [17–19]. To enhance the Curie temperature $T_C$ of this material, the addition of Co is the most suitable way. Moreover, Co can improve the glass-forming ability (GFA) of the materials.

In this work we replaced a part of Fe by Co in LaFe$_{11-x}$Co$_x$Si$_2$ ($x = 0, 1, 2, 3, 4$ and $5$) alloy ribbons. We can see that all samples are partly crystallized. The results of structure analyses also show that the phase formation clearly depends on the concentration of Co. Intensities of the diffraction peaks are gradually reduced with Co addition. There are two diffraction peaks of the XRD patterns corresponding to $\alpha$-Fe phase. Other peaks are those of cubic NaZn$_{13}$-type phase [19].

Figure 2 represents thermomagnetization curves of the LaFe$_{11-x}$Co$_x$Si$_2$ ($x = 0, 1, 2, 3$ and $4$) alloy ribbons with an applied magnetic field of 12 kOe. We see that these ribbons have a magnetic phase transition in the range of 200–550 K. The magnetization decreases with increasing temperature and rapidly decreases at the magnetic phase transition. After the magnetic phase transition, the magnetization of all the ribbons does not reduce to zero but keeps at certain values characterized for the crystalline phase. This is suitable for the above structure analysis. It should be noted that Co-concentration strongly influences the Curie temperature of LaFe$_{11-x}$Co$_x$Si$_2$ ($x = 1, 2, 3, 4$ and $5$) ribbons. The Curie temperature is enhanced with increasing Co-concentration (see inset of figure 2). Without Co-addition, the magnetic phase transition of alloy is below room temperature. The $T_C$ value determined for the sample $x = 0$ is only $\sim 220$ K. However, when the concentration of Co is $1$ at $\%$, the phase transition temperature is raised to 315 K. As for the samples with $x = 2, 3$ and $4$, the $T_C$ values are $410, 480$ and $530$ K, respectively (see table 1). The effect of Co-addition on Curie temperature has a significant effect in controlling the working temperature of the magnetic refrigerants.

Figure 3 shows the dependence of magnetization on external field and Co-concentration of the ribbons at 300 K. From these hysteresis loops, both the saturation magnetization $M_s$ and the coercivity $H_c$ were obtained. All the samples manifest the soft magnetic behavior and their magnetization increases with increasing Co-concentration. Co increases saturation magnetization of the alloy (inset figure 3). This is due to the formation of LaCo$_{13}$ phase that increased with the addition of Co. The highest $M_s$ value of the alloy is above 100 emu g$^{-1}$ for $x = 4$. These two effects of Co furthermore improve capacity for application of the alloy in the magnetic refrigeration.
Table 1. Influence of Co concentration on magnetization at 12 kOe ($M_{12\text{kOe}}$), Curie temperature ($T_C$), maximum entropy change ($|\Delta S_M|_{\text{max}}$), full-width at half-maximum (FWHM) of entropy change peak and refrigerant capacity (RC) of the LaFe$_{11-x}$Co$_x$Si$_2$ ($x = 0, 1$ and $2$) alloy ribbons ($\Delta H = 12$ kOe).

| $x$ (%) | $M_{12\text{kOe}}$ (emu g$^{-1}$) | $T_C$ (K) | $|\Delta S_M|_{\text{max}}$ (J kg$^{-1}$ K$^{-1}$) | FWHM (K) | RC (J kg$^{-1}$) |
|---------|-------------------------------|------------|---------------------------------|------------|-----------------|
| 0       | 45                            | 220        | 1.43                            | 55         | 79              |
| 1       | 77                            | 315        | 1.25                            | 67         | 84              |
| 2       | 99                            | 410        | 1.26                            | 70         | 88              |
| 3       | 105                           | 480        | -                               | -          | -               |
| 4       | 111                           | 530        | -                               | -          | -               |

Figure 3. Hysteresis loops at 300 K of LaFe$_{11-x}$Co$_x$Si$_2$ ($x = 0, 1$, $2$, $3$ and $4$) ribbons. The inset shows magnetization at field of $12$ kOe versus Co concentration of these samples.

Figure 4. Thermomagnetization curves in various magnetic field of LaFe$_2$Co$_x$Si$_2$ ribbon. The inset shows magnetization versus magnetic field at 300 K obtained from virgin magnetic (dir.) and thermomagnetization (ind.) curves.

With the goal of finding magnetocaloric materials that possess magnetic transition temperature close to room temperature, we chose three samples of LaFe$_{11-x}$Co$_x$Si$_2$ ribbons with Co concentration in the range of $0–2$ at.% to investigate their MCE. We calculate magnetic entropy change ($\Delta S_M$) based on thermomagnetization data (figure 4). We can derive from thermomagnetization curves in different magnetic fields of the samples to be magnetized versus magnetic field curves at various temperatures (figure 5). To check this derivation procedure, we compared data (indirect data) deduced from thermomagnetization curve with data (direct data) of virgin magnetization ones (see inset of figure 4). We found that the data obtained from the two different ways coincided. Then the magnetic entropy change, $\Delta S_M$, is determined from $M(H)$ data by using equation (1).

By using the proposed method to calculate the magnetic entropy change of magnetocaloric materials, we can save time and expenditure for experiments. This method is also useful to avoid the effect of thermal fluctuation of measurement systems.

Figure 5. Magnetization versus magnetic field at various temperatures deduced from thermomagnetization curves of LaFe$_2$Co$_2$Si$_2$ ribbon.

Figure 6. $\Delta S_M(T)$ curves ($\Delta H = 12$ kOe) of LaFe$_{11-x}$Co$_x$Si$_2$ ($x = 0$, $1$ and $2$) ribbons. The inset indicates refrigerant capacity (RC) versus Ni-concentration of the alloy.
RC values determined for the samples with $x = 0, 1$ and 2 are 1.43, 1.25 and 1.26 J kg$^{-1}$ K$^{-1}$ and 55, 67 and 70 J kg$^{-1}$, respectively (see Table 1). One can see that the sample with Co concentration of 1 at.% has quite large $|\Delta S|^\text{max}$ and RC at around room temperature. This shows a capability to apply this kind of magnetocaloric materials in practice.

4. Conclusion

The magnetic and magnetocaloric properties in LaFe$_{11-x}$Co$_x$Si$_2$ ($x = 0, 1, 2, 3$ and $4$) alloy ribbons have been studied. Glass forming ability of the alloy can be enhanced considerably by the addition of Co. Curie temperature of the alloy can be regulated in room temperature region by replacement of a part of Fe by Co. The quite high maximum magnetic entropy change ($|\Delta S|^\text{max} > 1.2$ J kg$^{-1}$ K$^{-1}$ with $\Delta H = 12$ kOe), large refrigerant capacity (RC $> 80$ J kg$^{-1}$) and wide working range around room temperature (FWHM $> 60$ K) reveal application potential of this alloy in magnetic refrigeration technology.

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References

[1] Tegus O, Brück E, Buschow K H J and de Boer F R 2002 Nature 415 150
[2] Zhou X, Li W, Kunkel H P and Williams G 2004 J. Phys.: Condens. Matter 16 L139
[3] Tegus O, Fuquan B, Dagula W, Zhang L, Brück E, Si P Z, de Boer F R and Buschow K H J 2005 J. Alloys Compounds 396 6
[4] Medeiros L G, Oliveira N A and Troper A 2010 J. Alloys Compounds 501 177
[5] Krenke T, Duman E, Acet M, Wassermann E F, Moya X, Manosa L and Planes A 2005 Nature Mater. 4 450
[6] Phan M H, Peng H X and Yu S C 2007 J. Magn. Magn. Mater. 316 562
[7] Nam D N H, Dai N V, Hong L V, Phuc N X, Yu S C, Tachibana M and Takayama-Muromachi E 2008 J. Appl. Phys. 103 043905
[8] Zhang X, Zhang B, Yu S, Liu Z, Xu W, Liu G, Chen J, Cao Z and Wu G 2007 Phys. Rev. B 76 132403
[9] Phan T L, Duc N H, Yen N H, Thanh P T, Dan N H, Zhang P and Yu S C 2012 IEEE Trans. Magn. 48 1381
[10] Kovac J, Svec P and Skorvanek I 2008 Rev. Adv. Mater. Sci. 18 533
[11] Zeng H, Kuang C, Zhang J and Yue M 2012 Nanosci. Methods 1 16
[12] Wua D, Xue S, Frenzel J, Eggeler G, Zhai Q and Zheng H 2012 Mater. Sci. Eng. A 534 568
[13] Hu F, Shen B, Sun J and Chang Z 2001 Appl. Phys. Lett. 78 23
[14] Si L, Ding J, Li Y, Yao B and Tan H 2002 Appl. Phys. A 75 535
[15] Franco V, Blázquez J S and Conde A 2006 J. Appl. Phys. 100 064307
[16] Du J, Zheng Q, Li Y B, Zhang Q, Li D and Zhang Z D 2008 J. Appl. Phys. 103 023918
[17] Dong Q Y, Shen B G, Chen J, Shen J, Wang F, Zhang H W and Sun J R 2009 J. Appl. Phys. 105 053908
[18] Wang F W, Zhang X X and Hu F X 2000 Appl. Phys. Lett. 77 1360
[19] Yan A, Muller K H and Gutfleisch O 2008 J. Alloys Compounds 450 18