Study of magnetocaloric effect in $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys prepared by different cooling methods

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Abstract. $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys are annealed at 1503 K for 5 h and cooled down to room temperature by furnace cooling, air cooling and quenching in ice water, respectively. The main phases are 1:13 phases in those alloys. The impurity phases are α -Fe and the amount of LaFeSi phase is so small that it is hard to observe in their XRD patterns. The powder X-ray diffraction patterns and SEM show that the three cooling methods have little influence on the phase relation and microstructure of those $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys. But the lattice constant of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloy prepared by quenching in ice water is lesser than those of the other two alloys, respectively. For studying the influence of different cooling processes on magnetic properties, the Curie temperature, thermal and magnetic hysteresis, magnetocaloric effect and relative cooling power are investigated. The result shows that the Curie temperature of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ prepared by quenching in ice water is 197.6 K, about 4 K lesser than those of the other two $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys. The maximum $\Delta S_M(T, H)$ of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ prepared by furnace cooling and quenching in ice water is the most and the least under the field of 0–2 T, respectively.

Keywords. $\text{LaFe}_{13-x}\text{Si}_x$ alloys; magnetocaloric materials; microstructure; high-temperature annealing; cooling methods.

1. Introduction

$\text{LaFe}_{13-x}\text{Si}_x$ alloys with $1.1 \leq x \leq 1.6$ shows a giant magnetocaloric effect and have been studied in detail (Fujita *et al* 1999, 2003, 2009, 2011; Hu *et al* 2001; Shen *et al* 2009; Morrison *et al* 2010). Because of the low price of starting materials and excluded deleterious elements, $\text{LaFe}_{13-x}\text{Si}_x$ alloys are the most promising magnetic refrigerants. However, this series of alloys have some disadvantages in practical application. One of the important points is that NaZn₁₃-type structure (hereafter 1:13 phase) in $\text{LaFe}_{13-x}\text{Si}_x$ alloys is hard to obtain directly from common solidification process due to the intrinsic incompleteness of a peritectic reaction: $\gamma\text{-Fe} + \text{L} \rightarrow \text{La}(\text{Fe}, \text{Si})_{13} (\tau_{1a})$, which often results in the mixed microstructure of $\alpha\text{-Fe} + \text{La}(\text{Fe}, \text{Si})_{13} (\tau_{1a}) + \text{LaFeSi} (\tau_4)$ (Raghavan 2001). In as-cast $\text{LaFe}_{13-x}\text{Si}_x$ alloys with a low Si ratio, there is almost no 1:13 phase. The $\text{LaFe}_{13-x}\text{Si}_x$ alloys with 1:13 phase are usually prepared by long time annealing from several days to several weeks between 1173 and 1373 K and then quenching rapidly in medium. Although some references reported that there were foreign phases (such as $\alpha\text{-Fe}$) in $\text{LaFe}_{13-x}\text{Si}_x$ alloys prepared

by this method (Mandal *et al* 2005; Gao *et al* 2009; Shen *et al* 2010), most researches can obtain $\text{LaFe}_{13-x}\text{Si}_x$ alloys with single NaZn₁₃-type structure (Fujita *et al* 2001; Chen *et al* 2003; Hu *et al* 2003; Fujita and Fukamichi 2005; Sun *et al* 2006). To shorten the annealing time, the melt-spun and over 1473 K high-temperature annealing methods and so on are used to prepare $\text{LaFe}_{13-x}\text{Si}_x$ alloys (Liu *et al* 2004; Fujita and Fukamichi 2005; Gutfleisch *et al* 2005; Yan *et al* 2005, 2008; Zhu *et al* 2005; Chen *et al* 2011). The cooling methods in those preparations are usually furnace cooling to room temperature and the annealing time is largely reduced to a few minutes or a few hours. However, almost all annealed $\text{LaFe}_{13-x}\text{Si}_x$ alloys prepared by those methods contain foreign phases. Slow cooling is believed to induce the lower-temperature phases, such as LaFeSi phase. On the other hand, the distance of atoms diffusion between $\alpha\text{-Fe}$ and LaFeSi phase becomes great with the peritectic reaction happening, in which several days or several weeks are required to complete solid-state diffusion reaction, especially when the annealing temperature is relatively low. Thus, $\alpha\text{-Fe}$ and LaFeSi phases may come from the incompleteness of peritectoid reaction when the annealing time is not long enough. Therefore, the point that slow cooling is believed to induce lower-temperature phases deserves further discussion.

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Up to now, no elaborate study of the influence of different cooling processes on the phase relation and microstructure of $\text{LaFe}_{13-x}\text{Si}_x$ alloys has been reported. In this paper, $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys are annealed at 1503 K for 5 h followed by furnace cooling, air cooling and quenching in ice water down to room temperature, respectively. The influence of three cooling processes on the phase relation, microstructure, and magnetic properties was investigated, respectively.

2. Experimental

~10 g polycrystalline $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys buttons were fabricated by conventional arc melting in a high purity argon atmosphere using high purity (La: 99.4 wt%, Fe: 99.9 wt% and Si: 99.9999 wt%) elements and the alloys were remelted five times to achieve a homogeneous composition. According to our result in high-temperature and short-time preparation, 1503–1523 K are the optimal temperatures to prepare 1:13 phase (Chen *et al* 2011). The melted alloys were sealed in an evacuated quartz tube filled with 18,000 Pa high purity argon. The samples were annealed at 1503 K for 5 h in a high-temperature resistance furnace. The heating speed is 10 K/min in 273–400 K range and 15K/min in 400–1503 K range, respectively. After annealing, the sample was cooled down to room temperature by furnace cooling, air cooling and quenching in ice water, respectively. The phase purity and crystal structures were determined by powder X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation (Dandong DX-2600). Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) observations were carried out by Hitachi-S-3400N. Magnetic measurements were performed using a vibrating-sample magnetometer (VSM, Lakeshore 7410). Curie temperature (T_C) was determined from the maxima of dM/dT of the M - T curves, which were measured in an applied magnetic field of $H = 0.02$ T. The magnetic entropy changes $\Delta S_M(T, H)$ were calculated from isothermal magnetization curves (M - H curves) under magnetic fields up to 2 T in the vicinity of the Curie temperature using the thermodynamic Maxwell relation.

3. Results and discussion

Figure 1 shows XRD patterns of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys annealed at 1503 K (5 h) and cooled down to room temperature by furnace cooling, air cooling and quenching in ice water, respectively. By analysing and indexing X-ray diffraction patterns of the three samples, one can find that the main phases are 1:13 phase and a small amount of α -Fe solid solution exists in those alloys cooled by the above three methods. LaFeSi phase cannot be observed in their XRD patterns. From the angle of XRD patterns there are same phase relations, which indicates that above

three cooling processes have little influence on the relation phase in XRD patterns.

For future studies the effect of cooling methods on the amount of 1:13 phase, the quantitative analysis of 1:13 and α -Fe phases was studied by K -value method. According to K -value method, in sample including the needed to be measured phase and mixed reference phase (Al_3O_2), the mass percentage of the needed to be measured phase are

$$x_j = \frac{x_c I_j}{K_C^j I_C}, \quad (1)$$

where K_C^j is the strength ratio of the highest peak in X-ray pattern between the needed to be measured phase and that the referenced Al_3O_2 phase when they are mixed in 50 wt% proportions, it is also called as RIR-value. I_j and I_C are the strengths of the highest peak of the needed to be measured phase and referenced Al_3O_2 phase in X-ray pattern, respectively. x_c is the mass percentage of the mixed reference phase (Al_3O_2)/ Al_3O_2 phase. For the above mentioned $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys, there are only 1:13 and α -Fe phases, their mass percentage are:

$$x_{\alpha\text{-Fe}} = \frac{x_c I_{\alpha\text{-Fe}}}{K_C^{\alpha\text{-Fe}} I_C}, \quad (2)$$

$$x_{1:13} = \frac{x_c I_{1:13}}{K_C^{1:13} I_C}, \quad (3)$$

by using (2) and (3), we obtain

$$\frac{x_{\alpha\text{-Fe}}}{x_{1:13}} = \frac{x_c I_{\alpha\text{-Fe}}}{K_C^{\alpha\text{-Fe}} I_C} \bigg/ \frac{x_c I_{1:13}}{K_C^{1:13} I_C} = \frac{I_{\alpha\text{-Fe}}}{I_{1:13}} \frac{K_C^{1:13}}{K_C^{\alpha\text{-Fe}}} = \alpha. \quad (4)$$

Because there are only 1:13 and α -Fe(Si) phases in sample, $x_{\alpha\text{-Fe}} + x_{1:13} = 1$. Thus

$$\frac{x_{\alpha\text{-Fe}}}{x_{1:13}} = \frac{1 - x_{1:13}}{x_{1:13}} = \frac{1}{x_{1:13}} - 1 = \alpha,$$

$$\left. \begin{aligned} x_{1:13} &= \frac{1}{1 + \alpha} \\ x_{\alpha\text{-Fe}} &= 1 - \frac{1}{1 + \alpha} = \frac{\alpha}{1 + \alpha} \end{aligned} \right\}. \quad (5)$$

$\ln \alpha = (I_{\alpha\text{-Fe}} / I_{1:13})(K_C^{1:13} / K_C^{\alpha\text{-Fe}})$, the value of $K_C^{\alpha\text{-Fe}}$ is 10.76. However, the value of $K_C^{1:13}$ has not been reported. We find the diffraction peak strengths of 1:13 phase to be almost the same to those of LaCo_{13} phase on the same measured condition. Thus, the value of $K_C^{1:13}$ is alternated by that of $K_C^{\text{LaCo}_{13}}$ and its value is 4.28. Combined with X-ray patterns, the values of $I_{\alpha\text{-Fe}}$ and $I_{1:13}$ can be easily obtained.

Figure 1. XRD patterns of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys annealed at 1503 K for 5 h and followed by three cooling methods to room temperature, respectively.

Table 1. Lattice constant, T_C , ΔS_M , thermal and magnetic hysteresis and RCP.

Cooling methods	Lattice constant	T_C (K)		$ \Delta S_{\max} $ (J/kg K)	Hysteresis (J/kg)		
		Heating process	Cooling process		Thermal	Magnetic	RCP (J/kg)
Furnace cooling	11.46037(3) Å	201.7	196.2	17.7	4.5 K	17.7 (200 K)	144.2
Air cooling	11.46005(5) Å	201.6	198.2	15.7	3.4 K	17.8 (200 K)	141.6
Quenching	11.45097(2) Å	197.6	192.2	14.9	5.4 K	12.7 (199 K)	138.8

According to the above method, we find that the percentages of 1:13 phase are 95.9, 95.7 and 96.0 wt% in $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys prepared by furnace cooling, air cooling and quenching in ice, respectively. It indicates that above three cooling methods almost have no influence on the mass percentage of 1 : 13 phase. But from table 1, one can find that the values of lattice constant of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys prepared by quenching in ice water are lower than those of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys prepared by furnace cooling and air cooling. At the same time, the main diffraction peaks of 1 : 13 phase of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys quenched in ice water have obvious shift to high angle, as shown in figure 1. This is a sign of lattice contraction and is in harmony with the lattice constants, as shown in table 1.

Figure 2 demonstrates backscattered SEM micrographs of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys annealed at 1503 K (5 h) and cooled by the above three different cooling methods down to room temperature, respectively. The different microstructures in these alloys can be identified by XRD and EDS analyses. One can find that the phase relation

and the amount of different phases are in agreement with XRD patterns as is shown in figure 1. The microstructures of black α -Fe and white LaFeSi phases in the $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys cooled by furnace cooling or air cooling are not greater than that of the alloy cooled by quenching in ice water. It also shows that the three cooling methods mentioned above have little influence on the microstructure of different phases.

3.1 Magnetic property

Figures 3(a–c) displays temperature dependent magnetization measured under 0.02 T in heating and cooling processes for $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys annealed at 1503 K (5 h) and followed by furnace cooling, air cooling and quenching down to room temperature, respectively. T_C is defined as the maximum of dM/dT in heating process. Results show that there are differences in T_C of those alloys prepared by different cooling processes. T_C of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys quenched in ice water is 195.4 K, and is about 4 K

Figure 2. Backscattered SEM micrographs of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys annealed at 1503 K for 5 h and followed by three cooling methods down to room temperature.

Figure 3. Temperature dependent magnetization measured under 0.02 T on heating and cooling processes for $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys.

less than those of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys prepared by furnace cooling and air cooling. We know that lattice expansion will lead to a stronger Fe–Fe exchange interaction and then increase T_C in $\text{La}(\text{Fe}, \text{Si})_{13}$ systems. Above result shows that the lattice constant of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys prepared by quenching in ice water is the least, which results in Fe–Fe exchange interaction and is the weakest in the three alloys. Thus, T_C of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloy quenching in ice is lesser than those of the other two alloys, respectively. Temperature hysteresis is defined as the difference between T_C (heating process) and T_C (cooling process). From figures 3(a–c), one can find that the three alloys have the temperature hysteresis phenomenon and the values of thermal hysteresis are shown in table 1. The thermal hysteresis of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys quenching in ice water is almost reaches 5.4 K.

The isothermal magnetization curves measured at different temperatures in the vicinity of T_C are shown in figures 4(a–c) for three $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys. The measurements were performed in field increasing process. In order to check whether the isothermal magnetization process involves magnetic hysteresis, parts of M – H curves were measured during magnetic field up and down near T_C . There is a field-induced itinerant-electron metamagnetic (IEM) transition from the paramagnetic state to ferromagnetic state above T_C , which leads to a sharp increase of magnetization as the applied field exceeds a certain value. The magnetic hysteresis loss, which is defined by the area enclosed by the ascending and descending branches of magnetization curve are shown partly in table 1. The value of magnetic hysteresis is in response to the first-order magnetic transition intensity to a certain extent. The magnetic hysteresis losses of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloy cooled by quenching in ice water is only 12.7 J/kg at 199 K, which is lower than those at 200 K of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys cooled by furnace cooling and air

cooling. Figure 5 shows Arrott plots of three $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys near T_C . According to I–S model, negative slope in Arrott plots curve often indicates a first-order transition and the linear relation in Arrott plot above T_C implies that a second-order magnetic transition occurs. The samples exhibit an obvious negative slope, which confirms further the first-order magnetic transition characteristic.

Figure 4. Magnetization isotherms of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys measured under field of 0–2 T.

Because the first-order magnetic refrigerant materials have magneto-elastic coupling or magneto-volume coupling characteristic and PM and FM phases coexist at the temperature close to the phase transition, there still exists the issue about whether the Maxwell equations are suited to calculate the magnetic entropy change of those materials (Giguère *et al* 1999). Some researchers pointed that a first-order phase transition occurred in a finite temperature range and two phases may coexist in the transition process. In this case, the Maxwell relation could yield a spurious ΔS_M peak in the vicinity of the Curie temperature T_C . Considering the fact that magnetic field affects only the magnetic state of PM phase, which coexists with FM phase near T_C , only PM phase contributes to the

Figure 5. Arrott plots for samples of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys.

Figure 6. Magnetic entropy change, $\Delta S_M(T, H)$, as functions of temperature of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys.

thermal effect. Some references used Clausius–Clapeyron equation to calculate ΔS_M . But Sun *et al* (2000) pointed out that the Maxwell relation and the Clausius–Clapeyron equation can give similar magnetic entropy change for an idealized first-order transition. Currently, the magnetic entropy measurements (via the Maxwell relation) are widely used. In our work, ΔS_M of three $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys were calculated by using the Maxwell relation. From the curves for ΔS_M vs temperature under magnetic field changes of 0–2 T, as is shown in figure 6, there is no spurious ΔS_M peak near T_C , as in Liu *et al* (2007). The three cooling methods have certain influence on ΔS_M , the values of maximum $\Delta S_{M,\max}$ are 17.7, 15.7 and 14.9 J/kg K for three $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys prepared by furnace cooling, air cooling and quenching in ice water, respectively. In addition, because the experimental field is higher than at least H_C of field-induced IEM transition, $\Delta S_M(T, H)$ peaks have asymmetrical broad phenomenon at higher temperature above T_C .

To obtain high-performance magnetic refrigerants, it is important to evaluate the quantity of heat transferred by magnetic refrigerant materials. The relative cooling power (RCP) defined by the following expression is one of the measurements (Pecharsky and Gschneidner 1999):

$$\text{RCP} = -\Delta S_{m,\max} \times \delta T,$$

where $\Delta S_{m,\max}$ and δT are the negative maximum values of ΔS_M and the temperature width of half maximum of ΔS_M , respectively. The values of RCP obtained from figure 6 for $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys prepared by furnace cooling, air cooling and quenching in ice water are 143.2, 141.6 and 138.8 J/kg, respectively. It indicates that the three cooling methods have little influence on RCP, the values of RCP are all about 140 J/kg.

4. Conclusions

The three cooling methods of furnace cooling, air cooling and quenching in ice water were used to prepare the $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys. XRD patterns and SEM show that different cooling methods have little influence on the phase relation, microstructure and mass percentage of 1:13 phase. But the three cooling methods have obvious influence on the lattice constant and magnetic properties. The lattice constant, T_C and the value of maximum $\Delta S_{M,\max}$ of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys prepared by quenching in ice water are lesser than those of the other two $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys. From the refrigerator ability angle, the three cooling methods have little influence on RCP. The relative cooling power (RCP) of $\text{LaFe}_{11.5}\text{Si}_{1.5}$ alloys prepared by furnace cooling, air cooling and quenching in ice water are 143.2, 141.6 and 138.8 J/kg, respectively.

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