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High-temperature phase transition and magnetic property of $LaFe_{11.6}Si_{1.4}$ compound

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ABSTRACT

The $LaFe_{11.6}Si_{1.4}$ compounds are prepared by arc-melting and then annealed at different high temperatures from 1323 K(5 h) to 1623 K(2 h). The powder X-ray diffraction and metallographic microscopy show that 1423 K and 1523 K are two curial temperatures, at which large amount of 1:13 phase begins to form and the most amount of 1:13 phase is obtained, respectively. With annealing temperature increasing to 1573 K and 1623 K, a new phase of La_5Si_3 is detected in $LaFe_{11.6}Si_{1.4}$ compound. According to the DSC curve of as-cast $LaFe_{11.6}Si_{1.4}$ compound and the X-ray patterns of annealed $LaFe_{11.6}Si_{1.4}$ compounds, the high-temperature phase transition process is analyzed. For studying the influence of different high-temperature and short-time annealing on the Curie temperature, thermal and magnetic hysteresis, magnetocaloric effect of $LaFe_{11.6}Si_{1.4}$ compound annealed at different temperatures are also investigated.

1. Introduction

$LaFe_{13-x}Si_x$ compounds with $1.1 \le x \le 1.6$ are enjoying interest in the magnetic materials community due to the observation of a large MCE in $LaFe_{11.4}Si_{1.6}$ compound [1]. Those compounds undergo a first-order magnetic transition at T_C about 200 K, and an itinerant-electron metamagnetic (IEM) transition just above T_C [2,3], which result in a large magnetocaloric effect (MCE). Because of the low price of starting materials and excluding deleterious elements, $LaFe_{13-x}Si_x$ compounds are the hot research points in magnetic refrigerant materials field for long time [4–9]. Recently, the main studies about $LaFe_{13-x}Si_x$ compounds focused on how to enhance T_C, improve magnetocaloric properties, reduce the large thermal and magnetic hysteresis, and improve the corrosion resistant property. Researches found that the T_C can adjust according to the hydrogen content in $LaFe_{13-x}Si_x$ hydrides while the large magnetic entropy change is retained, and both thermal and magnetic hysteresis are remarkably reduced because of the weakness of the itinerant-electron metamagnetic transition after hydrogenation [10–12]. The doping of B as interstitial can help to form 1:13 phase in as-cast $LaFe_{13-x}Si_x$ B_y compounds accompanied Fe_2B phase appearance [13], and the thermal and magnetic hysteresis of $LaFe_{13-x}Si_x$ B_y compounds is less than that of mother alloys [14–16]. But the Fe_2B phase cannot be eliminated after the as-cast $LaFe_{13-x}Si_x$ B_y compounds being annealed and the magnetocaloric effect decrease. The corrosion behavior and inhibition corrosion of $La(Fe_{0.94}Co_{0.06})_{11.7}Si_{1.3}$ compound and $LaFe_{11.6}Si_{1.4}$ in different solutions have been investigated [17–19]. The result shows that these alkaline solutions is necessary to ensure that a protection film can be formed on the surface of metal and have a good inhibition effect on the $LaFe_{13-x}Si_x$ compounds in a certain. Although the $La(Fe_{1-x}Co_x)_{11.9}Si_{1.1}$ compounds with $0.055 < x < 0.122$ produced by powder metallurgy, $La(Fe0_{.745}Co_{0.17}Si_{0.085})_{13}$ ribbons prepared by melt spinning and annealed for a shorter time, and the $LaFe_{13-x}Si_x$ ($x = 1.4, 1.6, 1.8, 2.0$) series synthesized by high energy ball-milling have been investigated [20–22], most of $LaFe_{13-x}Si_x$ compounds with NaZn13-type structure (hereinafter 1:13 phase) are prepared by long time annealing for several weeks at between 1173 K and 1373 K, and then quenching rapidly in medium. In the $LaFe_{13-x}Si_x$ compounds, 1:13 phase is hard to be obtained directly from common solidification process due to the intrinsic incompleteness of a peritectic reaction: $\gamma\text{-Fe} + L \rightarrow La(Fe,Si)13(\tau_{1a})$, which often results in the mixed microstructure of $\alpha\text{-Fe} + La(Fe,Si)13(\tau_{1a}) + LaFeSi(\tau_4)$ [23]. For shorting the annealing time, some researchers used melt-spun or rapid quenching/short-time annealing at about 1273 K to prepare 1:13 phase [24–26]. Compared with the arc-melting/long time annealing, the annealing time reduces to a few minutes or a few hours, but the preparation process is more complex, and most of annealed $LaFe_{13-x}Si_x$ compounds contained a small amount of α-Fe phase. Recently, our group used the arc-melting/high-temperature and short-time annealing to prepare 1:13 phase, the result showed

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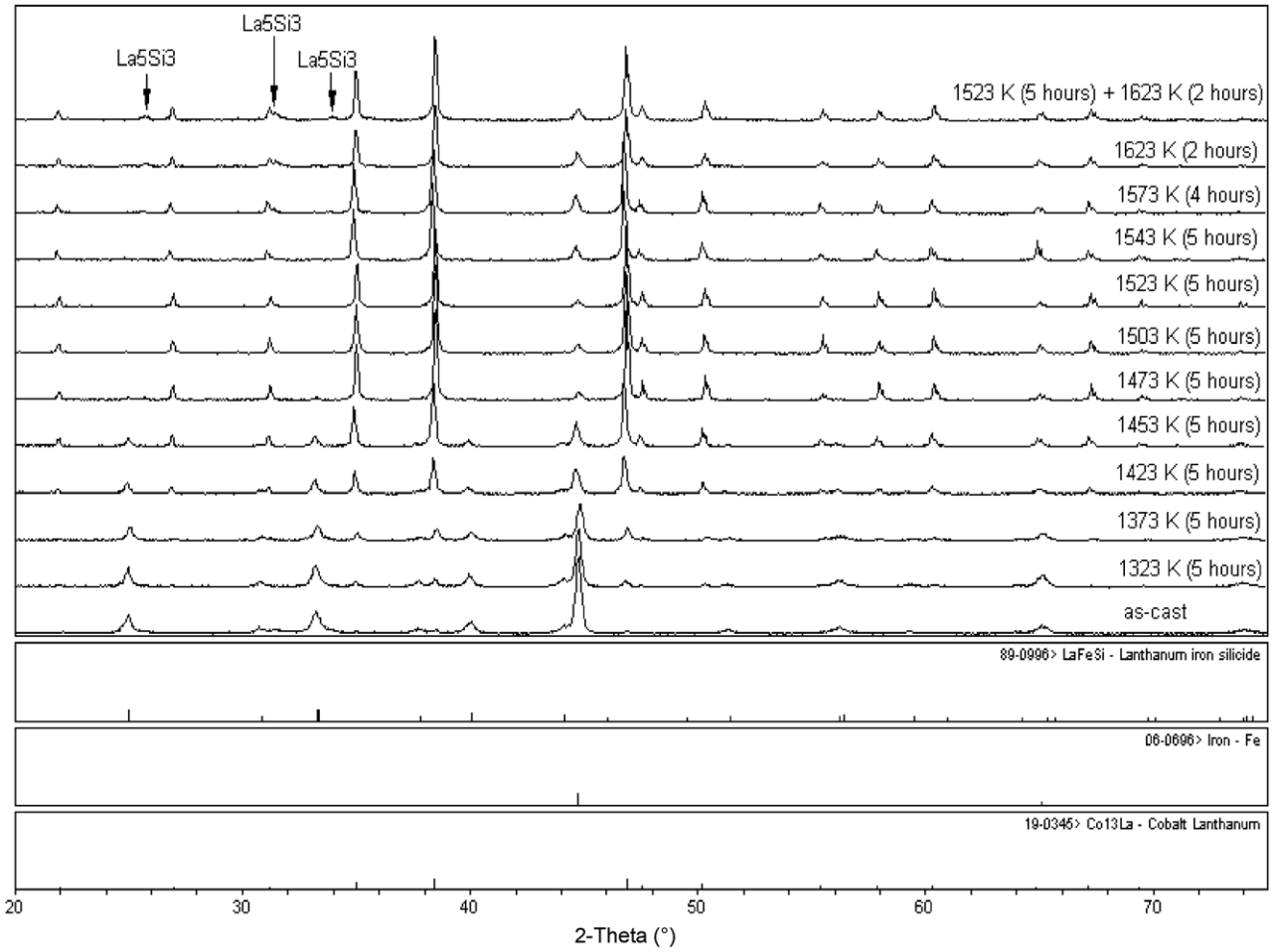


Fig. 1. XRD patterns of as-cast $LaFe_{11.6}Si_{1.4}$ compound and the annealed compounds at different high temperatures from 1323 K to 1623 K.

the samples also contained a small amount of α-Fe phase [27]. For further improving the preparation process of La(Fe, Si)$_{13}$ compounds, the study of high-temperature phase transition of as-cast La(Fe, Si)$_{13}$ compounds is necessary. Up to now, no elaborate study of the phase transition is made when the as-cast La(Fe,Si)$_{13}$ compounds are annealed.

In this paper, the influence of different short-time and high-temperature annealing of as-cast $LaFe_{11.6}Si_{1.4}$ compound from 1323 K to 1623 K on phase relation is investigated. According to the DSC curve of as-cast compound and the X-ray patterns of annealed compounds, the high-temperature phase transition process is analyzed. In addition, the phase relation, microstructure, thermal and magnetic hysteresis, and magnetocaloric effects of $LaFe_{11.6}Si_{1.4}$ compounds prepared by the two stages annealing are also studied.

2. Experimental details

Approximately 10 g polycrystalline $LaFe_{11.6}Si_{1.4}$ 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, the compounds were re-melted five times to achieve a homogeneous composition. The as-cast compounds were annealed as followed process: 1323 K for 5 h (hereinafter h), 1373 K(5 h),1423 K, 1453 K(5 h), 1473 K(5 h), 1503 K(5 h), 1523 K(5 h), 1373 K(2 h) + 1523 K(5 h), 1523 K(5 h) + 1373 K(2 h), 1543 K(5 h), 1573 K(4 h), 1623 K(2 h), 1523 K(5 h) + 1623 K(2 h), and 1373 K(2 h) + 1523 K(5 h), and 1523 K(7 h) + 1373 K(2 h), respectively, in a molybdenum wire furnace of 3×10^{-3} Pa vacuum, and then by furnace cooling down to room temperature. The phase purity and crystal structures observation were determined by powder x-ray diffraction (XRD) using Cu (K_α) radiation. Scanning electron microscope (SEM) and energy disperse spectroscopy (EDS) observation are carried by Hitachi-S-3400 N. The phase transition of the compound was studied by Differential Scanning Calorimetry (DSC) in Ar gas atmosphere from 300 to 1773 K at 10 K/min. Magnetic measurements were performed using a vibrating-sample magnetometer (VSM, Lakeshore 7410). The Curie temperature (T_C) were 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 ΔS_M (T, H) were calculated from isothermal magnetization curves (M–H curves) under a magnetic fields of 0–2 T in the vicinity of the Curie temperature using the thermodynamic Maxwell relation [28].

3. Result and discussion

3.1. The phase relation and microstructure of the single stage high-temperature and short-time annealing

The long time annealing at about 1323 K is often used to prepare the $LaFe_{13-x}Si_x$ compounds with 1:13 phase, detailed studies of the heat treatment of $LaFe_{13-x}Si_x$ compounds are reported in few articles. For studying the effect of different higher-temperature and short-time heat treatment on the phase relation of $LaFe_{11.6}Si_{1.4}$ compounds, different annealing temperatures were experimented. Fig. 1 shows the XRD patterns of $LaFe_{11.6}Si_{1.4}$ compounds annealed at different high temperatures from 1323 K to 1623 K, and the as-cast compound respectively. One can find that the as-cast $LaFe_{11.6}Si_{1.4}$ compound mainly consists of α-Fe and LaFeSi phases. In addition, the appearance of three minor peaks at $2\theta = 35$, 38.5, and 46.8 indicates that there is a small amount of the third phase crystallized as 1:13 phase. It is well known that the temperature of annealing is higher, and the speed of diffusion of atoms is just larger during the high-temperature and solid-phase diffusion reaction. Thus, with increasing of annealing temperature from 1323 K to 1423 K, the amount of 1:13 phase gradually increases and α-Fe

and LaFeSi phases gradually reduce. But compared the XRD patterns, one can find that the amount of 1:13 phase in the compound annealed at 1423 K is obviously more than that of other compounds annealed at lower temperatures. It indicates that 1423 K is a critical temperature to form 1:13 phase. The speed of phase transforming to form 1:13 phase is relative slow when the annealing temperatures are lower than 1423 K.

With the temperature increasing from 1423 K to 1523 K, α-Fe and LaFeSi phases in the $LaFe_{11.6}Si_{1.4}$ compounds reduce in turn. The LaFeSi phase is rarely observed in the XRD pattern when the annealing temperatures reach 1503 K and 1523 K. Although the α-Fe always exists in the $LaFe_{11.6}Si_{1.4}$ compounds, the amount of α-Fe is very small in the compounds annealed at 1503 K and 1523 K, especially at 1523 K. Thus, 1523 K is also a critical temperature for obtaining the 1:13 phase during the high-temperature and short-time annealing of as-cast $LaFe_{11.6}Si_{1.4}$ compound. Our result that there is a small amount of α-Fe besides 1:13 main phase in the XRD patterns is accordant to some references, which reported that the $La(Fe,Si)_{13}$ compounds prepared by annealing for long time and then quenching rapidly in medium or furnace cooling to room temperature also contained the 1:13 main phase and small amount of α-Fe [29–32]. This indicates that high-temperature and short-time annealing at 1523 K is an effective and feasible method to prepare $LaFe_{11.6}Si_{1.4}$ compounds with 1:13 phase.

To further observe the effect of annealing temperature on the phase relation, the as-cast $LaFe_{11.6}Si_{1.4}$ compounds are annealed at 1543 K(5 h), 1573 K(4 h), 1623 K(2 h), and 1523 K(5 h) + 1623 K(2 h), respectively. When the annealing temperature increases to 1573 K and 1623 K, there is a new phase crystallized as La_5Si_3 phase whose the strongest diffraction peak is at $2\theta = 31.5$, and more La_5Si_3 phase appears with higher annealing temperature. The $LaFe_{11.6}Si_{1.4}$ compound annealed at 1523 K(5 h) + 1623 K(2 h) also contains a certain amount of La_5Si_3 phase, which is not observed in the XRD pattern of $LaFe_{11.6}Si_{1.4}$ compound annealed at 1523 K(5 h). The amount of α-Fe in the $LaFe_{11.6}Si_{1.4}$ compounds annealed at 1573 K(4 h), 1623 K(2 h), and 1523 K(5 h) + 1623 K(2 h) is obviously more than that in the compound annealed at 1523 K(5 h). In addition, there is no diffraction peaks of La_5Si_3 phase in the compound annealed at 1543 K(5 h), but the amount of α-Fe is more than that of $LaFe_{11.6}Si_{1.4}$ compound annealed at 1523 K(5 h). In all, the most amount of 1:13 phase is obtained when the as cast $LaFe_{11.6}Si_{1.4}$ compounds is annealed at 1523 K among the above single stage annealing under the same time.

Fig. 2 demonstrates the backscattered SEM micrographs of the annealed $LaFe_{11.6}Si_{1.4}$ compounds and as-cast compound. The different phases in these compounds can be identified by XRD and EDS analysis. The phase relation and the amount of different phases are in agreement with the XRD patterns, as shown in Figs. 1 and 2. Through the refine analysis, we find the 1:13 phase locates between α-Fe and LaFeSi phase, but the amount is so small that it hard to be observed in the SEM micrographs of the annealed $LaFe_{11.6}Si_{1.4}$ at 1373 K(5 h) and as-cast compounds, as shown in Fig. 2(a) and (b). The SEM micrographs also shows that 1423 K and 1523 K are two critical temperatures during the high-temperature and short-time annealing of as-cast $LaFe_{11.6}Si_{1.4}$ compounds, at which large amount of 1:13 phase begins to form and the most amount of 1:13 phase is obtained, respectively.

3.2. The analysis of high-temperature phase transition of as-cast $LaFe_{11.6}Si_{1.4}$ compound

In order to study high-temperature phase transition during the annealing process, DSC measurement was performed. Fig. 3 shows the DSC curve of massive as-cast $LaFe_{11.6}Si_{1.4}$ compound during the heating process. There are four main endothermal peaks; the temperature of peaks is 1407.6 K, 1530.5 K, 1593.1 K, and 1739.3 K, respectively. In as-cast $LaFe_{11.6}Si_{1.4}$ compound, α-Fe is primary phase, $La(Fe,Si)_{13}$ is peritectic phase, and LaFeSi is solidifying phase of residual liquid, respectively. It is universally acknowledged that the 1:13 phase should be formed through γ-Fe and LaFeSi phase if the annealing temperature is higher than 1185 K, which is the temperature of structural transition between α-Fe and γ-Fe. Based on the analysis of EDS, we find that α-Fe in as-cast $LaFe_{11.6}$ $Si_{1.4}$ compound is Fe(Si) solid solution, the atomic percent of Fe and Si is 94.85 at% and 5.15 at%, respectively. In the Fe–Si binary phase diagram, there exists the phase transition between γ-Fe and α-Fe only when the Si at% is less than 3.8 at% in Fe(Si) solid solution [33]. Thus, there is only α-Fe during the annealing process of as-cast $LaFe_{11.6}Si_{1.4}$ compound, and the 1:13 phase is formed through $\alpha\text{-Fe} + \text{LaFeSi} \rightarrow La(Fe,Si)_{13}$. According to the phase rule, the melting point of α-Fe is the highest, that of LaFeSi phase is the lowest in as-cast $LaFe_{11.6}Si_{1.4}$ compound, and that of peritectic phase is between the melting point of primary phase (α-Fe) and the temperature of peritectic reaction. Combining with the Fe–Si binary phase diagram, one can easily come to the conclusion that 1739.3 K in the DSC curve is the melting point of Fe(Si) solid solution. Based on the result that large amount of 1:13 phase begins to form and the most amount of 1:13 phase is obtained when the as-cast $LaFe_{11.6}Si_{1.4}$ compound is annealed at 1423 K and 1523 K, respectively, 1407.6 K and 1530.5 K are the melting point of LaFeSi phase and the temperature of peritectic reaction: $\alpha\text{-Fe} + L \rightarrow La(Fe,Si)_{13}$, respectively. In addition, 1593.1 K is the melting point of 1:13 phase. Thus, when the annealing temperature is near 1593.1 K, the non-equilibrium freezing of liquid 1:13 phase leads to the appearance of La_5Si_3 phase.

The tradition method of preparing $LaFe_{11.6}$ $Si_{1.4}$ compound is by long-time annealing at about between 1173 K and 1373 K, and the annealing temperature is lower than melting point of LaFeSi phase (about the 1407.6 K). Under this situation, the 1:13 phase is formed through a peritectoid reaction between the α-Fe and the solid LaFeSi phases; it needs long time to complete solid state diffusion reaction. But when the annealing temperature is near the point of peritectic reaction, the 1:13 phase is formed through a peritectic reaction between the α-Fe and liquid phase, which is faster than the peritectoid reaction between α-Fe and solid state LaFeSi phase. Thus, there is the most amount of 1:13 phase in the $LaFe_{11.6}$ $Si_{1.4}$ compound annealed at 1523 K under the same annealing time.

3.3. The two stages high-temperature and short-time annealing

Combining the result that most amount of 1:13 phase is obtained when the as cast $LaFe_{11.6}Si_{1.4}$ compound is annealed at 1523 K in high-temperature and short-time annealing process with the traditional preparation method that the as-cast $La(Fe,Si)_{13}$ compound is annealed at about 1373 K for long time. Two stages annealing are carried, they are 1373 K(2 h) + 1523 K(5 h), and 1523 K(7 h) + 1373 K(2 h), respectively. The aims of annealing of low temperature (1373 K) and high temperature (1523 K) are increasing the chemic driving force and diffused driving force of phase transition, respectively. Figs. 4 and 5 are the XRD patterns and SEM micrographs of the $LaFe_{11.6}Si_{1.4}$ compounds annealed at 1523 K(5 h) and different two stages. Three compounds consist of the main 1:13 phase and a certain amount impurities. Although it is hard to be observed from XRD patterns, very small amount of LaFeSi phase (white phase) can be observed in SEM micrographs. In the SEM micrographs, the black phase (α-Fe) and white phase (LaFeSi) in $LaFe_{11.6}Si_{1.4}$ compound annealed at 1523K(7 h) + 1373K(2 h) are obviously less than that of others, which attributes to the annealing time at 1523 K is longer than others.

In traditional preparation method, the single 1:13 phase compounds are almost prepared through long time annealing and then quenched in ice water or liquid nitrogen, and slow cooling

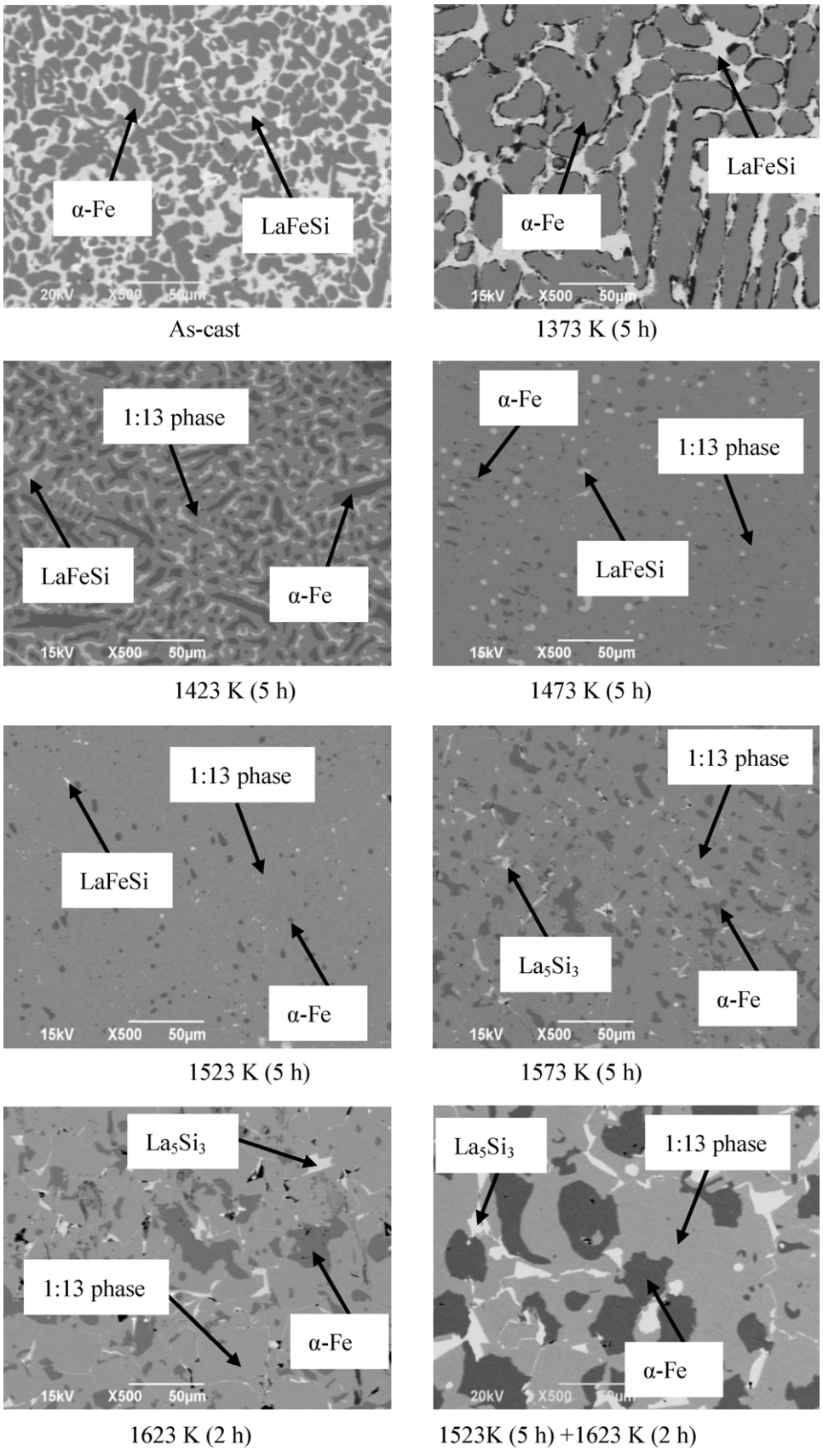


Fig. 2. Backscattered SEM micrographs of $LaFe_{11.6}Si_{1.4}$ compounds annealed at different high temperatures from 1323 K to 1623 K and as-cast compound.

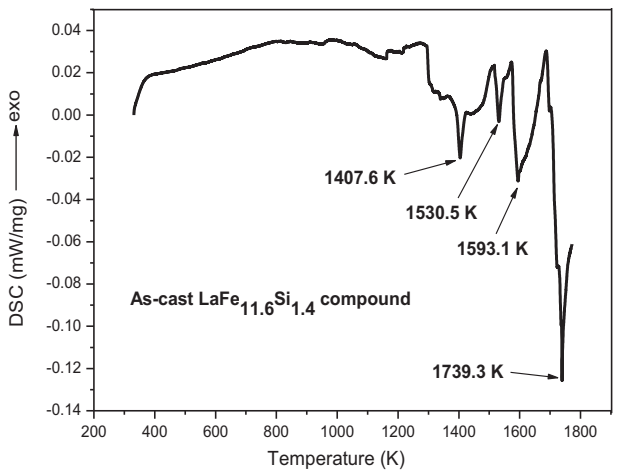


Fig. 3. DSC curve of as-cast massive $LaFe_{11.6}Si_{1.4}$ compound.

is believed to induce the lower-temperature phases, such as 1:1:1 phase. But in our work, LaFeSi phase in the compounds annealed at 1523 K(7 h) + 1373 K(2 h) is not more than that in the compound annealed at 1523 K(5 h). Thus, the LaFeSi phase also can come from the incompleteness of peritectoid reaction, and not the slow cooling process. Up to now, there has no report to discuss whether the α-Fe and LaFeSi phases come from the incompleteness of peritectoid reaction or the slow cooling process.

3.4. Magnetic property

Fig. 6(a–c) displays the temperature dependent magnetization measured under 0.02 T in heating and cooling processes for $LaFe_{11.6}Si_{1.4}$ compounds annealed at 1523 K(5 h), 1373 K(2 h) + 1523 K(5 h), and 1523 K(7 h) + 1373 K(2 h), respectively. T_C is defined as the point of the maximum of dM/dT in heating process. The difference of above three compounds' T_C is little, they are about 190 K. Temperature hysteresis is an important index for magnetic refrigeration material, and it is defined as the difference between T_C (heating process) and T_C (cooling process). To some extent, the value of temperature hysteresis is response to the first-order magnetic transition intensity. From Fig. 6(a–c), one can find that three compounds have the temperature hysteresis phenomenon, and the value is about 2 K. The isothermal magnetization curves measured at different temperature in the vicinity of T_C are shown in Fig. 7(a–c) for three $LaFe_{11.6}Si_{1.4}$ compounds. The measurements were performed in field increasing process. In order to check whether the isothermal magnetization process involves magnetic hysteresis, one of M–H curves was measured during field up and down at near T_C. There is a field-induced itinerant-electron metamagnetic (IEM) transition from the paramagnetic state to the ferromagnetic state in the range of 2 K above T_C. It indicates that the initiated critical field (H_C) of field-induced IEM transition is lower than 2 T. Magnetic hysteresis is also response to the first-order magnetic transition intensity, which is defined as the enclosed area between the ascending and descending branches of magnetization curve. The magnetic hysteresis loss of compounds annealed at 1523 K(5 h) and 1373 K(2 h) + 1523 K(5 h) is smaller than that of compound annealed at 1523 K(7 h) + 1373 K(2 h), their value are 36.5, 39.7, and 46.8 J/kg, at 189, 190, and 191 K, respectively. Fig. 8 shows the compared Arrott plots of the samples. One can find that negative slopes appear in all samples, and the value of slope increases in sequential order. According to the 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. Thus, all samples have

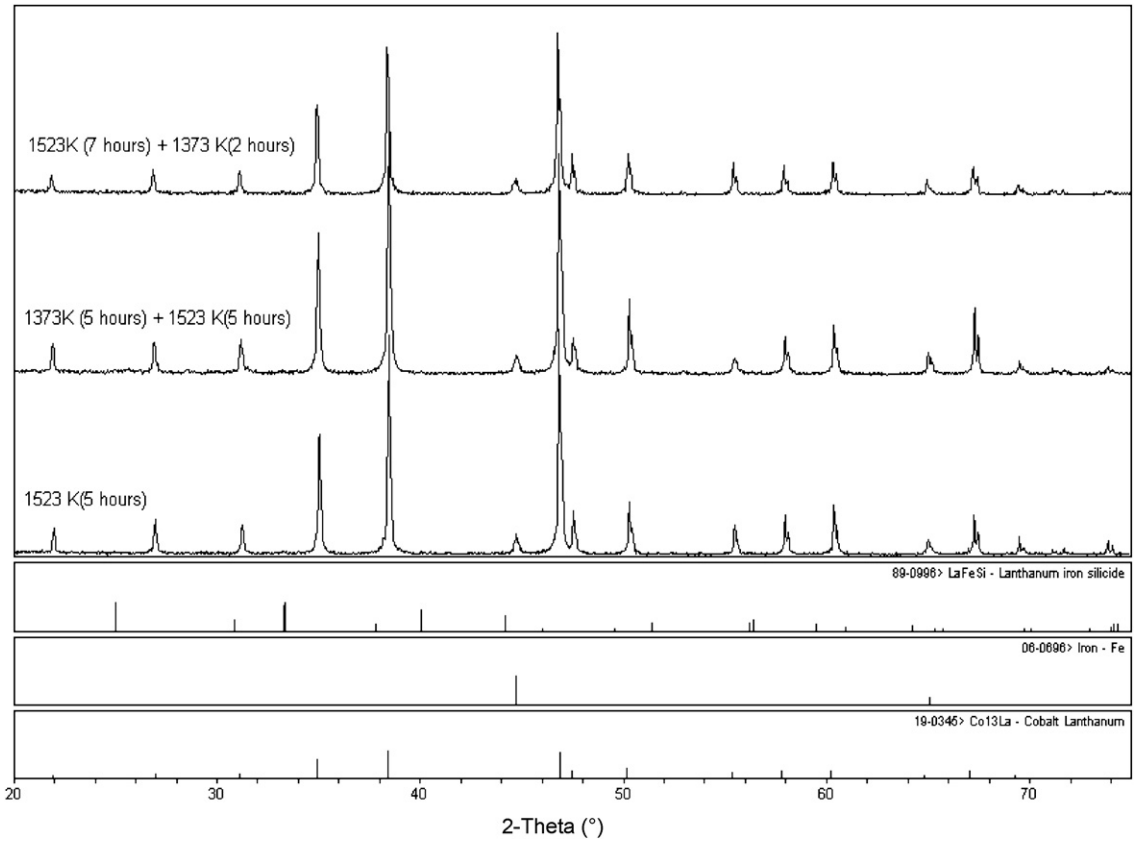
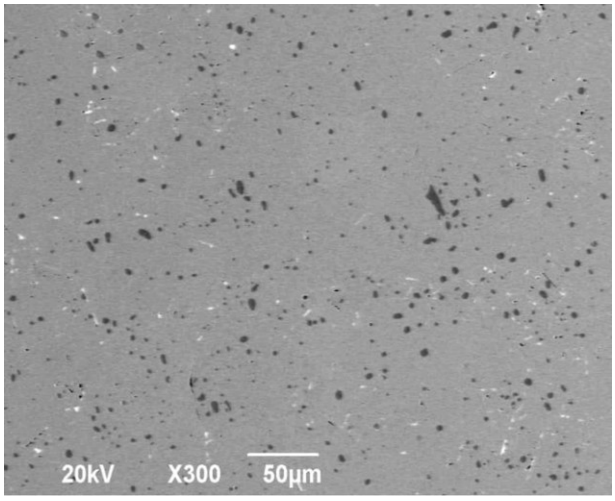
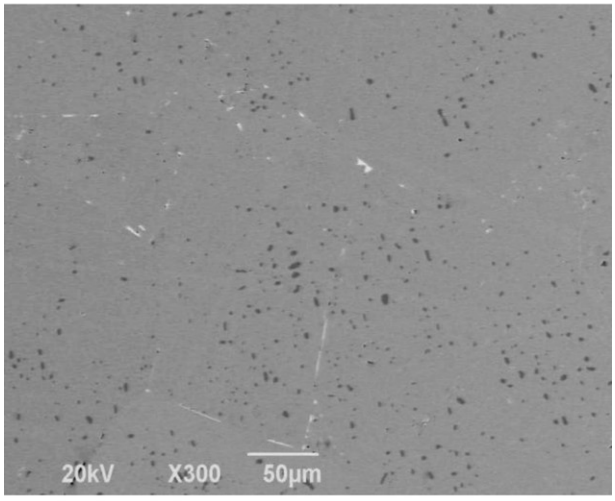


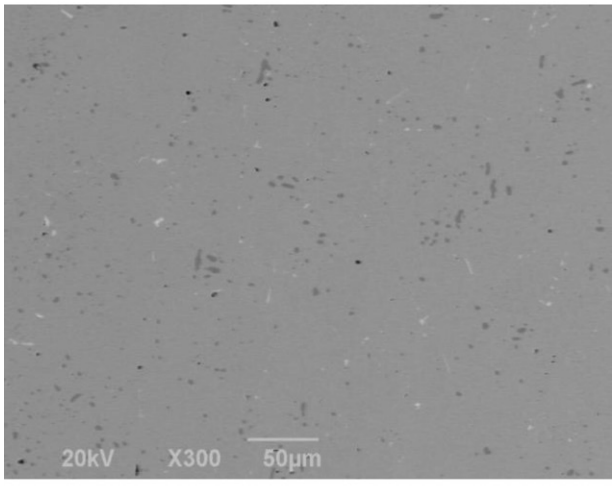
Fig. 4. XRD patterns of $LaFe_{11.6}Si_{1.4}$ compounds after being annealed at 1523 K(5 h), 1373 K(2 h) + 1523 K(5 h), and 1523 K(7 h) + 1373 K(2 h), respectively.



1523 K(5 h)

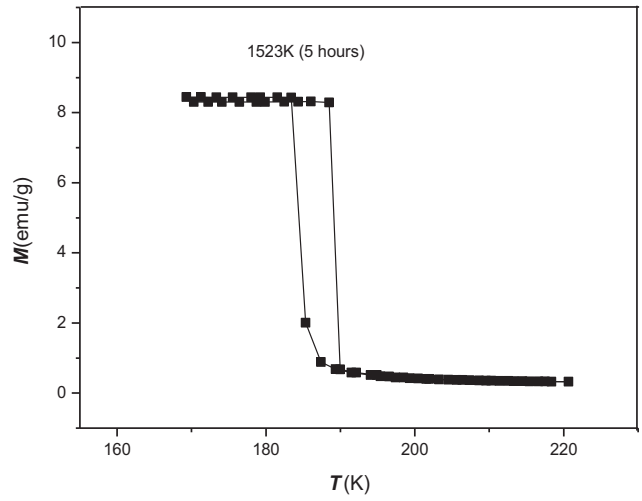


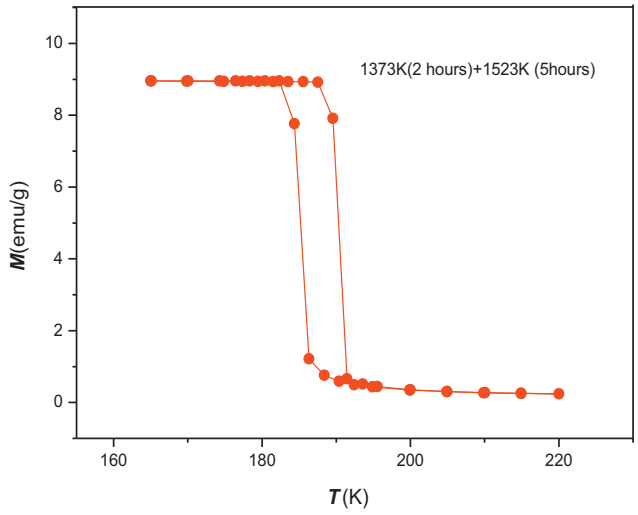
1373 K(2 h)+1523 K(5 h)



1523 K(7 h)+1373 K(2 h)

Fig. 5. Backscattered SEM micrographs of $LaFe_{11.6}Si_{1.4}$ compounds after being annealed at 1523 K(5 h), 1373 K(2 h) + 1523 K(5 h), and 1523 K(7 h) + 1373 K(2 h), respectively.





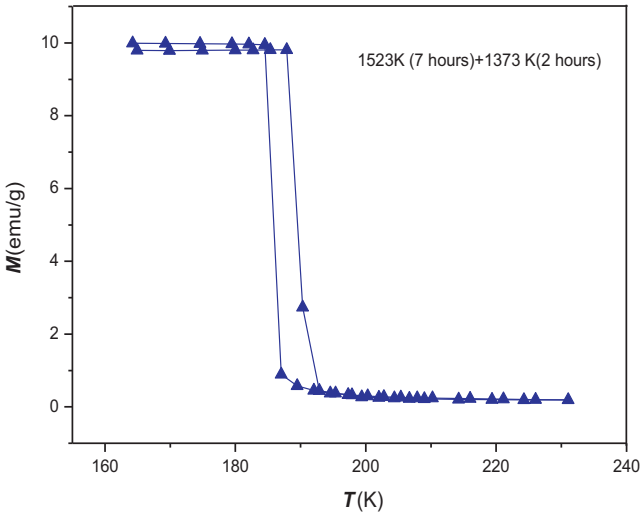
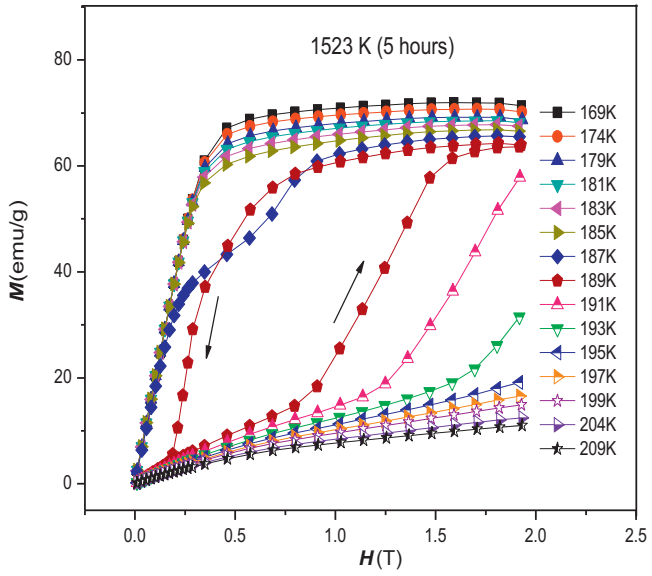
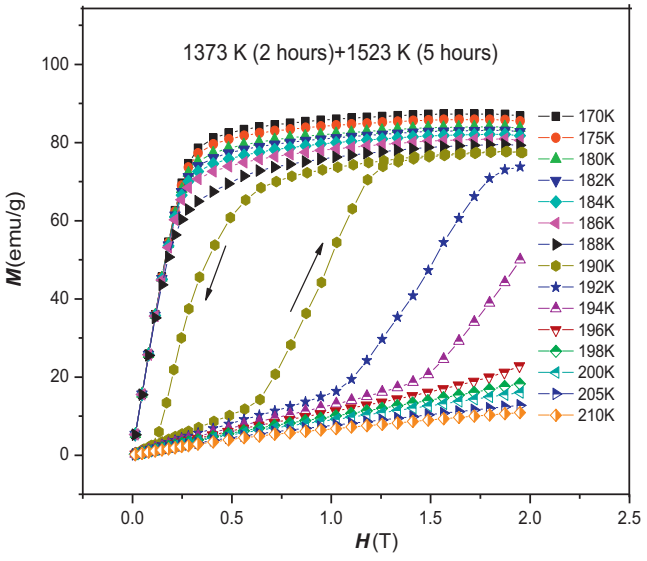


Fig. 6. Temperature dependent magnetization measured under 0.02 T on heating and cooling processes for $LaFe_{11.6}Si_{1.4}$ compounds.

the first-order of magnetic transition behavior, and the first-order of magnetic transition behavior becomes intensity in sequential order.

Because the first-order magnetic refrigerant materials have magnetoelastic coupling or magnetovolume coupling characteristic, there still exists the issue about whether the Maxwell equations





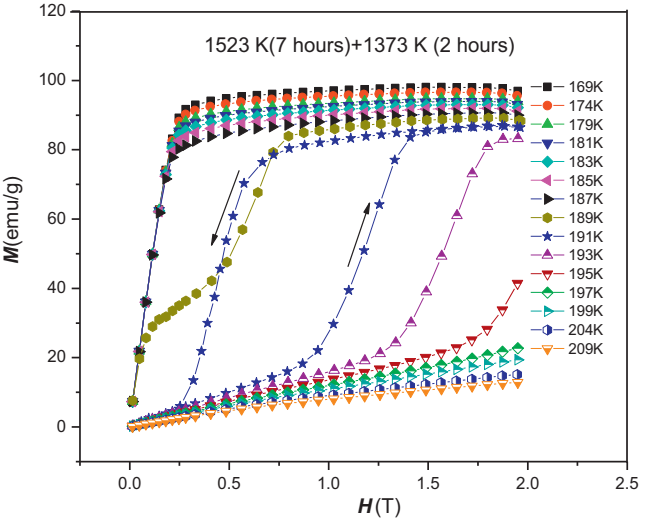


Fig. 7. Magnetization isotherms of $LaFe_{11.6}Si_{1.4}$ compounds measured under field of 0-2 T.

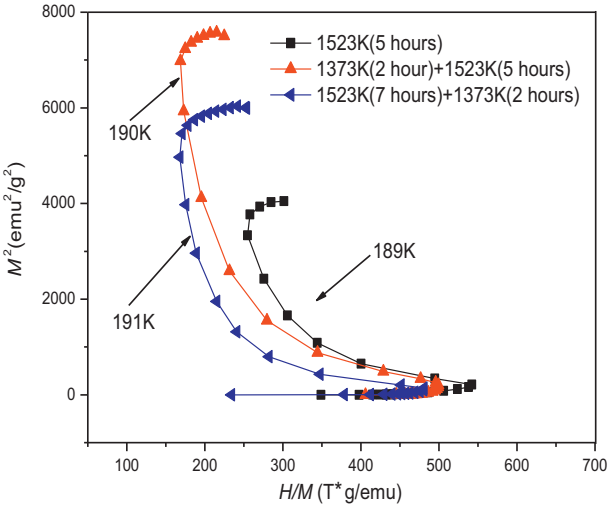


Fig. 8. Arrott plots for samples of $LaFe_{11.6}Si_{1.4}$ compounds.

suits to calculate the magnetic entropy change of those materials. Sun et al. pointed out that the Maxwell relation and the Clausius–Clapeyron equation can give similar magnetic entropy change for an idealized first-order transition [5,34]. But in reality, a first-order phase transition occurs 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 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 the FM phase near T_C, only the PM phase contributes to the thermal effect. Liu et al. established a modified equation for calculating ΔS in reference [31]: $\Delta S[(T_1 + T_2)/2] = \sum_1/(T_1 - T_2)$. Fig. 9 shows the ΔS_M (T, H) calculated by using Maxwell relation based on the magnetization data as functions of temperature and magnetic field for $LaFe_{11.6}Si_{1.4}$ annealed by different processes. Because the experimental field is higher than the H_C of field-induced IEM transition, ΔS_M (T, H) peaks have asymmetrical broad phenomenon to higher temperature above T_C. The value of maximum ΔS_M (T, H) is 18.5, 21.5, and 25.3 J/kg K for three compounds near T_C, the change trend of maximum ΔS_M (T, H) is same to the first-order behavior of the magnetic transition in compounds. But from the M–H curves, as shown in Fig. 7, one can find that the compound

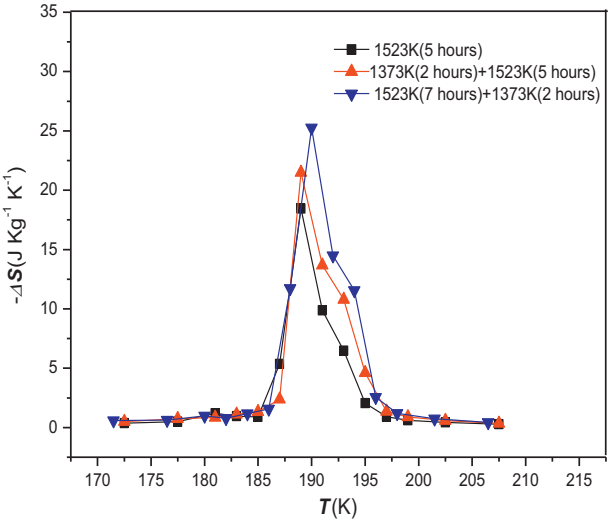


Fig. 9. Magnetic entropy change ΔS_M (T, H) as functions of temperature of $LaFe_{11.6}Si_{1.4}$ compounds.

$LaFe_{11.6}Si_{1.4}$ present a mixed magnetic phase in the temperature range near T_C, especially in the samples annealed at 1523 K(5 h) and 1523 K(7 h) + 1373 K(2 h). Thus, the use of the Maxwell relation for the evaluation of the entropy change close to the magnetic transition is not valid. More realistic values of the entropy change can be obtained based on the approaches developed in Ref. [35]. The result showed realistic values of the entropy change near T_C obtained as in Ref. [35] is 11.3 and 17.8 J/kg K for 1523 K(5 h) and 1523 K(7 h) + 1373 K(2 h), respectively, they are smaller than those obtained by using the Maxwell relation. In addition, according to the Fe–Si binary phase diagram, the Curie temperature of α-Fe(Si) is far higher than room temperature, α-Fe(Si) is at ferromagnetic state and has no the magnetic transition between ferromagnetic and paramagnetic. Thus, the magnetic entropy change of α-Fe(Si) is very small during magnetization and demagnetization process, and it is negligible in the calculation of the magnetic entropy change ΔS in this work.

4. Conclusions

Combining the DSC of as-cast massive $LaFe_{11.6}Si_{1.4}$ compound with the X-ray patterns of $LaFe_{11.6}Si_{1.4}$ compounds annealed at different high temperatures from 1323 K(5 h) to 1623 K(2 h), the high temperature phase transition process is analyzed. Large amount of 1:13 phase begins to form in $LaFe_{11.6}Si_{1.4}$ compounds when the annealing temperature is higher than the melting point of LaFeSi phase (about the 1407 K). Because 1523 K is close to the temperature of peritectic reaction: α-Fe + L → La(Fe, Si)13, thus the most amount of 1:13 phase is obtained in the $LaFe_{11.6}Si_{1.4}$ compounds annealed at 1523 K under the same annealing time. The non-equilibrium freezing of liquid 1:13 phase leads to the appearance of La_5Si_3 phase when the annealing temperature is near the melting point of 1:13 phase. The phase relation and microstructure of the $LaFe_{11.6}Si_{1.4}$ compounds annealed at 1523 K(5 h), 1373 K(2 h) + 1523 K(5 h) and 1523 K(7 h) + 1373 K(2 h), show that longer annealing time is helpful to decrease the impurity phases, especially at 1523 K. The magnetic measurement shows that above three compounds keep the first-order of magnetic transition behavior at T_C (about 190 K). The values of the maximal magnetic entropy change $\Delta S_M(T, H)$ obtained by Maxwell relation are 18.5, 21.5, and 25.3 J̃ kg K, respectively under the field of 0–2 T.

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