Microstructure and Magnetocaloric Effect by Doping C in La-Fe-Si Ribbons

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Abstract: The melt-spun ribbons of LaFe_{11.5}Si_{1.5}C_{x} (x = 0, 0.1, 0.2, 0.3) compounds are prepared by the melt fast-quenching method. The doping of C is beneficial to the nucleation and precipitation of the La (Fe, Si)_{13} phase, which is indicated by the microstructure observation and the elemental analysis. Subsequently, the ribbons of LaFe_{11.5}Si_{1.5}C_{0.2} are annealed at different times, and the phase composition, the microstructures, and the magnetic properties are investigated. The LaFe_{11.5}Si_{1.5}C_{0.2} ribbons annealed at 1273 K for 2 h achieved the best magnetic properties, and the maximum isothermal magnetic entropy change with a value of 9.45 J/(kg·K) upon an applied field of 1.5 T at an increased Curie temperature 255 K.

Keywords: microstructure; magnetocaloric effect; rapid solidification; annealing; maximum isothermal magnetic entropy

1. Introduction

Magnetic refrigeration, as a new pollution-free and efficient refrigeration technology, has attracted widespread attention and systematic research [1]. Among the magnetic refrigeration materials currently developed, the LaFe_{13-x}Si_{x} (1.2 ≤ x ≤ 1.6) alloy is a promising candidate because of its large magnetocaloric effect, low cost, and environmentally friendly properties [1–6]. However, there are still some issues, such as the low Curie/working temperature and the long annealing time to generate the La (Fe, Si)_{13} phase producing the large magnetocaloric effect, that hinder this kind of material from practical applications. At present, transition elements such as Co [7,8] and Ni are widely used to replace Fe, or elements such as B [9], H [10], and C [11–13] with a small atomic radius can be doped as interstitial atoms to improve the Curie temperature of the La-Fe-Si alloy. The addition of a few rare earth elements, such as Ce instead of La, can greatly improve the magneto-thermal performance of the LaFe_{13-x}Si_{x} alloy, but there is the problem of the Curie temperature reduction. Although Co replacing Fe can improve the Curie temperature of the La-Fe-Si alloy, the maximum isothermal magnetic entropy change of the alloy is reduced significantly [14]. Furthermore, the H element is doped as gap atoms in the La-Fe-Si alloy, while the Curie temperature increases, but the hydride is chemically unstable above 330 K, which is an unavoidable problem in practical applications [15].

In 2016, the structural and magnetothermal properties of the LaFe_{13-x}Si_{x}C_{y} carbide were investigated by V. Paul-Boncour et al. [16], who found that C atom doping leads to an increase in the Curie temperature and a drastic decrease of the magnetic entropy change. An almost single 1:13 phase was obtained after only a 30 min of heat treatment at 1393 K for the ball-milled samples. Even though doping C in the La-Fe-Si alloy ingot can increase the Curie temperature and obtain the optimal magnetic properties with a maximum isothermal magnetic entropy 12.7 J/(kg·K) (ΔH = 5 T) [17,18], the alloy ingot needs a long-time heat treatment for around 1 week for the formation of the La (Fe, Si)_{13} phase. Therefore, in order to increase the Curie temperature and reduce the heat-treatment
time simultaneously, we investigated melt-spun ribbons of LaFe$_{11.5}$Si$_{1.5}$C$_x$ ($x = 0, 0.2$) compounds prepared using the melt fast-quenching method. The formation of La (Fe, Si)$_{13}$ phase in solidification and subsequent heat treatments by doping C was studied using an X-ray diffraction analyzer. The magneto-thermal properties were systematically studied using a vibration sample magnetometer.

2. Experimental Details

The raw materials used in this experiment were Fe (purity not less than 99.55%), La (purity not less than 99.9%), Si (purity not less than 99.999%), and graphite (purity not less than 99.9%). Considering the volatile rare earth elements in the melting process, the burn loss of the rare earth element La was measured by 10%. To make the sample composition uniform, electromagnetic stirring was initiated during the melting process and each sample was flipped and melted four times. The ingots were melt and spun into ribbons using a melt-spinner with a copper wheel at a surface speed of 35 m/s. For the subsequent heat treatment in a muffle furnace, the melt-spun ribbons were sealed in glass tubes filled with inert gas. The heat-treatments at a temperature of 1273 K to the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ ribbons were 3 min and 2 h, respectively.

The phase structure analysis to the melt-spun ribbons was conducted by an X-ray diffraction instrument, D/MAX-2200-type (Cu target, K$_\alpha$-ray). The magnetic properties were determined by a vibration sample magnetometer, namely the Lakeshore7470. The thermal magnetic curve was tested under the 0.1 T magnetic field. The isothermal magnetization curve was tested under the 0–1.5 T magnetic field. The magnetic entropy variation was calculated using the Maxwell Equation (1).

\[ \Delta S_M(T, H) = S_M(T, H) - S_M(T, H = 0) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH \]  

3. Result and Discussions

3.1. Nucleation Rate and Phase Structure

Figure 1a shows the XRD pattern of unannealed LaFe$_{11.5}$Si$_{1.5}$C$_x$ ($x = 0, 0.1, 0.2, 0.3$) ribbons. It is not hard to see from the XRD pattern that in the fast-spun ribbons of LaFe$_{11.5}$Si$_{1.5}$C$_x$ ($x = 0.2$) compounds without heat treatment, the main phases are all $\alpha$-(Fe, Si) phases, and only a small amount of La (Fe, Si)$_{13}$ phases are contained. With the increase in C content, the relative content of the NaZn$_{13}$ type phase with a magnetocaloric effect increases first and then decreases, and the relative content of the La (Fe, Si)$_{13}$ phase reaches a maximum in the sample of $x = 0.2$. With the continued increase in C content, the relative content of the La (Fe, Si)$_{13}$ phases tended to decrease. The doping of C favors the formation of the La (Fe, Si)$_{13}$ phases in the LaFe$_{11.5}$Si$_{1.5}$C$_x$($x = 0, 0.1, 0.2$, and 0.3) alloy. This is because during the rapid solidification process, the La (Fe, Si)$_{13}$ phase competed with the $\alpha$-(Fe, Si) phase, while the doping of C favored the shaped nucleus and the dissolution of the La (Fe, Si)$_{13}$ phase.

According to the analysis of the jade software, the 2θ of the main peak of the La (Fe, Si)$_{13}$ phase in the unannealed LaFe$_{11.5}$Si$_{1.5}$C$_x$ ($x = 0, 0.1, 0.2, 0.3$) alloy was 46.762°, 46.677°, 46.642°, and 46.512°, respectively, as well as with the doping of the C element. According to the Bragg formula $2dsin\theta = \lambda$ (d is the interplanar spacing, $\theta$ is the diffraction half angle, $\lambda$ is the wavelength), it can be seen that the interplanar spacing of the La (Fe, Si)$_{13}$ phase in the alloy rapid quenching band was increasing, which shows that C atoms as interstitial atoms entered the lattice of the La (Fe, Si)$_{13}$ phase of the NaZn$_{13}$ cubic structure, which caused the expansion of the crystal structure and the increase of the lattice constant. The results are shown in Table 1.
With the increase in C content, the relative content of the La (Fe, Si)$_{13}$ phase decreased. The doping C was beneficial to the nucleation and precipitation of the La (Fe, Si)$_{13}$ phase in the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ ribbons, because there was a competitive nucleation relationship between the La (Fe, Si)$_{13}$ phase and the $\alpha$-(Fe, Si) phase during rapid solidification.

The heterogeneous nucleation rate \[ I = \frac{k_B T N_{\alpha}}{3\pi \eta(T)a_0^3} \cdot \exp\left[-\frac{\Delta G^*}{k_B T}\right] \] \[ (2) \]

Figure 1b,c shows the nucleation rates of the $\alpha$-(Fe, Si) and La (Fe, Si)$_{13}$ phases versus the under-cooling degree at different C contents. During the solidification process of the ribbons, the degree of under-cooling affects the phase formation mechanism of the La-Fe-Si alloy. Figure 1b shows that in the solidification process of the La-Fe-Si alloy, the nucleation rate of the $\alpha$-(Fe, Si) phase is higher than that of the La (Fe, Si)$_{13}$ phase when the under-
cooling degree is small. Thus, the lower under-cooling degree is not conducive to the formation of the La (Fe, Si)$_{13}$ phase, and the main phase of the alloy is the $\alpha$-(Fe, Si) phase. When the over cooling degree is large, the shaped nucleus rate of the La (Fe, Si)$_{13}$ phase is higher than the $\alpha$-(Fe, Si) phase, facilitating the formation of more La (Fe, Si)$_{13}$ phases. The results show that the undercooling degree affects the competitive precipitation of the La (Fe, Si)$_{13}$ phase and $\alpha$-(Fe, Si) phase.

Under certain chamber pressure, the faster quenching speed, that is, the larger undercooling degree, creates conditions for the nucleation and precipitation of the La (Fe, Si)$_{13}$ phase, which is beneficial to the effective formation of the La (Fe, Si)$_{13}$ single phase. Secondly, the large undercooling degree during rapid solidification is conducive to the formation of a small La-Fe-Si alloy microstructure [21]. The non-equilibrium rapid solidification process in the La-Fe-Si ribbons provides a high degree of undercooling for the nucleation and precipitation of the La (Fe, Si)$_{13}$ phase, which induces the primary precipitation of the competitive La (Fe, Si)$_{13}$ phase. Meanwhile, the crystal structure of the $\alpha$-(Fe, Si) phase and La-Fe-Si phase grows slowly, and the nanoscale $\alpha$-(Fe, Si) phase is distributed periodically and uniformly, which is beneficial to the diffusion of La, Fe, and Si atoms during heat treatment and promotes the inclusion reaction of the La (Fe, Si)$_{13}$ phase. Therefore, the single-phase La (Fe, Si)$_{13}$ phase can be obtained only in a short time by using a fast quenching method to prepare La-Fe-Si alloy rapid quenching strips.

In Figure 2a, region I is small, corresponding to the La (Fe, Si)$_{13}$ phase when $x = 0$, and region II is the $\alpha$-(Fe, Si) phase. The regions between region I and region II are the transition regions. Figure 2b shows that region I (La (Fe, Si)$_{13}$ phase) is significantly increased when $x = 0.2$. Figure 2c is an enlarged diagram of region II, and Figure 2d is an enlarged diagram of the transition region. Table 2 is the EDS analysis of the micro-structure of the La-Fe-Si alloys. With the increasing C content, the content change of each element is not obvious.

![Figure 2](image-url)
Figure 3. X-ray diffraction patterns of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ ribbons at a wheel speed of 35 m/s annealed at 1273 K for different times. As is seen in Figure 4a, the free surface of the ribbon after heat treatment for 2 h, the internal phase composition of the grain is close to the La(Fe, Si)$_{13}$ phase, and the analysis results are consistent with the results of the XRD in Figure 3. As the heat-treatment time increases from 3 min to 2 h, the relative content of the α-phase decreases. This is due to the inclusion reaction between the α-(Fe, Si) phase and the La(Fe, Si)$_{13}$ phase when the heat treatment of the ribbons is carried out at a temperature of 1273 K for 2 h.

3.2. LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ Heat Treatment

Table 2. The EDS analysis of the micro-structure of LaFe$_{11.5}$Si$_{1.5}$C$_{x}$ (x = 0, 0.2) alloys.

| Chemical Composition | La (at %) | Fe (at %) | Si (at %) | Phase          |
|----------------------|-----------|-----------|-----------|----------------|
| x = 0                |           |           |           |                |
| white point          | 14.28     | 70.58     | 15.14     | La(Fe, Si)$_{13}$ |
| dark gray            | 0         | 94.48     | 5.52      | α-(Fe, Si)     |
| gray white           | 34.36     | 32.65     | 33.09     | LaFeSi         |
| x = 0.2              |           |           |           |                |
| white point          | 13.87     | 71.14     | 14.99     | La(Fe, Si)$_{13}$ |
| dark gray            | 0         | 94.45     | 5.55      | α-(Fe, Si)     |
| gray white           | 33.64     | 32.97     | 33.39     | LaFeSi         |

Through the analysis of jade software, it is found that with the extension of heat treatment time, the 2θ of the main peak of the 13 phases of La(Fe, Si) in the fast quenched strip are 46.800°, 46.730°, and 46.698°, respectively. The main peak of La(Fe, Si)$_{13}$ phase shifts to a small angle, because with the increase in heat treatment time, C atoms are fully spaced from the lattice of the La(Fe, Si)$_{13}$ phase with a NaZn$_{13}$ cubic structure, which makes its lattice expand and causes the lattice constant of the La(Fe, Si)$_{13}$ phase to increase [22]. In addition, it can be clearly seen from the figure that the La(Fe, Si)$_{13}$ phase in the alloy has become the main phase when the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ strip is heat treated for 3 min. Compared with the alloy samples prepared by the traditional melting ingot method, the melt quenching process with a certain rapid quenching speed provides deep undercooling conditions for the formation of the La(Fe, Si)$_{13}$ phase in the peritectic reaction process. It promotes the competitive nucleation and precipitation of La(Fe, Si)$_{13}$ phase in the rapid solidification process, and the La(Fe, Si)$_{13}$ phase formed in the early stage and the
refined La (Fe, Si)\textsubscript{13} phase grains in the melt rapid quenching shorten the time required for inclusion reaction in the heat treatment process. The results in Table 3 show that the lattice parameters are 11.4985 Å, 11.5036 Å, and 11.5107 Å at a wheel speed of 35 m/s annealed at 1273 K for as spun, 3 min and 2 h, respectively. In other words, the longer annealing time, the bigger the expansion of the alloy lattice.

Table 3. Lattice parameters of annealed LaFe\textsubscript{11.5}Si\textsubscript{1.5}C\textsubscript{0.2} ribbons at 1273 K for different times.

| Annealing Time | Lattice Parameters (Å) |
|---------------|------------------------|
| as spun       | 11.4985                |
| 3 min         | 11.5036                |
| 2 h           | 11.5107                |

Figure 4 is a free surface SEM appearance of the LaFe\textsubscript{11.5}Si\textsubscript{1.5}C\textsubscript{0.2} fast quenching strip at 35 m/s at different times at a temperature of 1273 K. As is seen in Figure 4a, the free surface of the rapid quenching ribbon without heat treatment has a flat surface, no obvious branch crystal tissue, with cluster boundaries similar to the crystal boundary, probably due to the fast cooling speed and small grain size. After 3 min of heat treatment, some white particles of the rapid quenching ribbon began to precipitate through the EDS analysis (see Table 4). After the preliminary analysis of the research group, it can be inferred that the white particles are La\textsubscript{2}O\textsubscript{3} [23]. Through the energy spectrum analysis of the free surface grain after heat treatment (see Table 4), in the atomic percentage of each element at different times, the internal phase composition of the grain is close to the La (Fe, Si)\textsubscript{13} phase, and the analysis results are consistent with the results of the XRD in Figure 3. As can be seen from Figure 4c, in the free surface of the ribbon after heat treatment for 2 h, the triangle appearance has grown almost completely into a quadrilateral appearance, has spread over the whole surface, the crystal boundary is relatively flat, and the white particles of the La-rich phase are mostly distributed at the grain boundary of the circle particles, rarely at the quadrilateral crystal boundary.

Figure 4. SEM images of LaFe\textsubscript{11.5}Si\textsubscript{1.5}C\textsubscript{0.2} ribbons annealed at 1273 K for different times: (a) 0 min; (b) 3 min; (c) 2 h.
Table 4. Inside grains and white grains the EDS analysis of LaFe_{11.5}Si_{1.5}C_{0.2} ribbons at a wheel speed of 35 m/s annealed at 1273 K for different times.

| Heat Treatment Time | Area           | La (at%) | Fe (at%) | Si (at%) | O (at%) | C (at%) | Phase                        |
|---------------------|----------------|----------|----------|----------|---------|---------|------------------------------|
| 0 min               | I (white particles) | 9.11     | 74.82    | 7.43     | 4.97    | 3.66    | La_2O_3                      |
|                     | II (intracrystalline) | 11.84    | 72.56    | 10.94    | 0.08    | 4.58    | La(Fe, Si)_{13}              |
| 3 min               | I (white particles) | 15.28    | 49.74    | 6.36     | 21.63   | 6.99    | La_2O_3                      |
|                     | II (intracrystalline) | 11.73    | 71.62    | 11.01    | 1.33    | 4.31    | La(Fe, Si)_{13}              |
| 2 h                 | I (white particles) | 18.97    | 25.93    | 4.96     | 36.88   | 13.26   | La_2O_3                      |
|                     | II (intracrystalline) | 11.33    | 69.10    | 11.14    | 4.37    | 4.06    | La(Fe, Si)_{13}              |

Figure 5 shows the microstructure appearance image and high resolution image of LaFe_{11.5}Si_{1.5}C_{0.2} with a rapid quenching speed of 35 m/s and 3 min of heat treatment. Figure 5b is the Fourier transform of the lattice stripe of the circle region of Figure 5a, calibrated as the uniform La(Fe, Si)_{13} phase. Figure 5c is the Fourier transform of the lattice stripes of the Figure 5d white strips, labeled as a uniform La-Fe-Si phase. Figure 5e is the Fourier transform of the lattice stripe of the Figure 5a dark area, labeled as a uniform α-(Fe, Si) phase.

![Figure 5](image_url)

Figure 5. Selected area electron diffraction of LaFe_{11.5}Si_{1.5}C_{0.2} ribbons after heat treatment for 3 min. (a) Display of selected area in TEM; (b) Fourier transform at the SAED of (a); (c) Fourier transform at the SAED of (d) white strips; (d) display of selected area in TEM; (e) Fourier transform at the SAED of (a–e).

Figure 6 shows the tissue appearance image and high resolution image of LaFe_{11.5}Si_{1.5}C_{0.2} with a fast quenching speed of 35 m/s and 2 h heat treatment. As can be seen from Figure 6a, the area in the fast quenching strip consists of two different shapes. Figure 6b is an enlarged picture of region 1. It can be found that the quadular bulge in the SEM diagram of the free surface is composed of small and uniform particles, the matrix consists of gray and white particles, with a particle size within 200–500nm, and the two shapes are distinguished by a straight boundary. The formation of a quadratic crystal boundary in Figure 4c is also confirmed.

![Figure 6](image_url)

Figure 6. Selected area electron diffraction of LaFe_{11.5}Si_{1.5}C_{0.2} ribbons after heat treatment for 2 h. (a) Display of selected area in TEM; (b) Fourier transform at the SAED of (a); (c) Fourier transform at the SAED of (d) white strips; (d) display of selected area in TEM; (e) Fourier transform at the SAED of (a–e).
Figure 6. (a,b) Microstructure morphology (c,f) HRTEM micro-graph; (d) Fourier transform; (e) display of selected area in TEM of 35 m/s LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ ribbons near the free surface annealed at 1273 K for 2 h.

From the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ fast quenched strip powder XRD pattern with a fast quenching speed of 35 m/s in Figure 3, the main phase is the La (Fe, Si)$_{13}$ phase, containing only a small number of $\alpha$-(Fe, Si) phases, so a large number of quadrilateral bumps in the free surface should be a relatively uniform La (Fe, Si)$_{13}$ phase and a small number of $\alpha$-(Fe, Si) phases in the white particles. A high-resolution morphology is taken at the junction of the base and the quadrilateral projection, as shown in Figure 6c. The Fourier transform of the lattice stripes of the high-resolution matrix A region is normalized to the uniform La (Fe, Si)$_{13}$ phase, the lattice stripe of the gray grain in the B, C region of a high resolution, and the raised gray particles to the La-Fe-Si phase.

3.3. Effects on the Magnetic Properties

As can be seen from Figure 7, with the extension of the heat treatment time, the Curie temperature of the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ quenching strip increases at 224 K (0 min), 231 K
(3 min), and 255 K (2 h). This is because, with the increase of heat treatment time, the lattice expansion of the NaZn$_{13}$ structure is caused by the effective entry of atomic energy into the gap position of La (Fe, Si)$_{13}$ phase C. The three strong peaks of the La (Fe, Si)$_{13}$ phase in Figure 3 can effectively prove this. With the C atoms entering the gap position in the La (Fe, Si)$_{13}$ lattice, the 3D band of the Fe becomes narrower, the ferromagnetic interaction is enhanced, and the curie temperature tends to increase obviously.

Figure 6. (a,b) Microstructure morphology (c,f) HRTEM micro-graph; (d) Fourier transform; (e) display of selected area in TEM of 35 m/s LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ ribbons near the free surface annealed at 1273 K for 2 h.

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Figure 7. Thermomagnetic curves of 35 m/s LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ ribbons annealed at 1273 K for different times.

Figure 8 shows the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ fast quenching strip with a fast quenching speed of 35 m/s at a temperature of 1273 K, the maximum isothermal temperature after different times of heat treatment. We can see from Figure 8 that when the heat treatment time is 0 min, 3 min, and 2 h, the maximum isothermal magnetic entropy change of the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ fast quenched strip is 2.32 J/(kg·K), 6.8 J/(kg·K), and 9.45 J/(kg·K), respectively. The maximum isothermal magnetic entropy change mutated after 20 min of heat treatment, and then showed an obvious trend of first increasing and then decreasing, and reached the maximum value after 2 h of heat treatment. This change in the magneto-thermal effect as the heat treatment time extends comes from the following reason. It is difficult to complete the crystallization reaction of the La (Fe, Si)$_{13}$ phase during solidification, and La-Fe-Si as the primary α-(Fe, Si) phase is the main phase in the fast-quenched strip of the alloy, and the relative content of the La (Fe, Si)$_{13}$ phase with a giant magnetothermic effect is relatively small, so it has a small maximum isothermal magnetic entropy change. After thermal treatment, during the wafer coating reaction process, the not fully reactive α-(Fe, Si) phase and the La-Fe-Si phase generates the La (Fe, Si)$_{13}$ phase, causing the La (Fe, Si)$_{13}$ phase in the alloy, thus having a large maximum isothermal magnetic entropy change, and mutations for the slightly longer thermal treatment (20 min). This agrees with the XRD result in Figure 3.

Figure 9 is the 3D curve of the temperature, magnetic field, and maximum isothermal magnetic entropy change of (x = 0.2) after thermal treatment for 2 h at 1273 K. As the magnetic fields increase, the ∆S−T curve changes from the symmetrical herringbone to the asymmetric curve, indicating that the alloy phase transition type from the secondary phase transition to the primary phase transition and ∆S shows an increasing trend (because the primary phase transition is the change of material magnetic ordered state caused by lattice distortion, the resulting magnetic entropy change is much greater than the secondary phase transition and reaches values of 9.45 J/(kg·K) upon an applied field of 1.5 T).
In the fast-quenched strip and the La-Fe-Si alloy, the magneto-thermal effect is improved, and the heat treatment time in the preparation process is greatly shortened by the melt fast quenching process. At the same time, the effects of different heat treatment times on the phase composition, magnetic properties, and micro-tissue of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ are also studied. We present the following conclusions:

- The doping of C promotes the formation of La (Fe, Si)$_{13}$ phases in the La-Fe-Si series alloy. Compared with La-Fe-Si alloy without C doping, the LaFe$_{11.5}$Si$_{1.5}$C$_x$ (x = 0.1, 0.2, 0.3) alloy obtained more of the La (Fe, Si)$_{13}$ phase without heat treatment.
- The process of heat treatment for 2 h at 1273 K facilitates a large isothermal variation of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ entropy of alloy. With the extended thermal treatment time, the maximum isothermal magnetic entropy change of the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ alloy fast strip tends to increase first before decreasing, reaching a maximum at 2 h of thermal treatment of 9.45 J/(kg·K).
- The characteristic quadrangle morphology in the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ alloy fast quenching strip with 2 h pf heat treatment is benefitted by obtaining a higher magneto-thermal effect. Through the transmission analysis, the quadrilateral convex appearance in the 2 h heat treatment is benefitted by obtaining a higher magneto-thermal effect. Through the transmission analysis, the quadrilateral convex appearance in the 2 h heat treatment is benefitted by obtaining a higher magneto-thermal effect.

4. Conclusions

Considering the disadvantages of the low magneto-thermal effect and the long heat treatment time of room temperature magnetic refrigeration materials using the La-Fe-Si alloy, the magneto-thermal effect is improved, and the heat treatment time in the preparation process is greatly shortened by the melt fast quenching process. At the same time, the effects of different heat treatment times on the phase composition, magnetic properties, and micro-tissue of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ are also studied. We present the following conclusions:

- The doping of C promotes the formation of La (Fe, Si)$_{13}$ phases in the La-Fe-Si series alloy. Compared with La-Fe-Si alloy without C doping, the LaFe$_{11.5}$Si$_{1.5}$C$_x$ (x = 0.1, 0.2, 0.3) alloy obtained more of the La (Fe, Si)$_{13}$ phase without heat treatment.
- The process of heat treatment for 2 h at 1273 K facilitates a large isothermal variation of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ entropy of alloy. With the extended thermal treatment time, the maximum isothermal magnetic entropy change of the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ alloy fast strip tends to increase first before decreasing, reaching a maximum at 2 h of thermal treatment of 9.45 J/(kg·K).
- The characteristic quadrangle morphology in the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ alloy fast quenching strip with 2 h pf heat treatment is benefitted by obtaining a higher magneto-thermal effect. Through the transmission analysis, the quadrilateral convex appearance in the 2 h heat treatment is benefitted by obtaining a higher magneto-thermal effect.

Figure 8. (a) $\Delta S$–T curves and (b) histogram of the maximum isothermal magnetic entropy of LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ ribbons at a wheel speed of 35 m/s annealed at 1273 K for different times.

Figure 9. 3D curve of the temperature, magnetic field, and maximum isothermal magnetic entropy variation of the LaFe$_{11.5}$Si$_{1.5}$C$_{0.2}$ fast quenched band at 35 m/s (after 1273 K × 2 h heat treatment).
La-Fe-Si phase, which facilitates the contact between the \(\alpha\)-(Fe, Si) phase and the La-Fe-Si phase, and promotes the packet analysis reaction. The uneven \(\alpha\)-(Fe, Si) phase white large particles distributed in the alloy strip during 5 min heat treatment are difficult to contact using La-Fe-Si during heat treatment, which is not conducive to the packet analysis reaction, so the magneto-thermal effect is poor.

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