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Effect of annealing pressure on surface oxidation in annealing process for LaFe$_{11.5}$Si$_{1.5}$C$_{0.13}$ strips

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ABSTRACT

La(Fe,Si)$_{13}$-based compounds are promising refrigerants for new magnetic refrigeration technology. Cumulatively, rapid solidification is one of the most effective synthetic methods for these compounds because it requires a short annealing time. However, the strips were found to become more susceptible to external factors due to the reduced dimensionality. In this work, the effect of annealing pressure on the surface oxidation of rapidly solidified LaFe$_{11.5}$Si$_{1.5}$C$_{0.13}$ strips during heat treatment is explored. The results show that a lower annealing pressure (5 × 10$^{-3}$ Pa) leads to obvious oxidation on the surface of the strip during the heat treatment. As a result, the chemical composition of the 1:13 phase becomes nonuniform on the strips after heat treatment. By annealing the strip composed of almost the single 1:13 phase under lower annealing pressure, the 1:13 phase is also decomposed because of oxidation. On the contrary, no obvious oxide layer is observed on the surface of the strip with the increase in the annealing pressure to 1 atm during the heat treatment. Additionally, the magnetic measurements show that the maximum magnetic entropy change ($|\Delta S|_{\text{max}}$) becomes smaller due to surface oxidation. The strips annealed under a higher annealing pressure exhibit a higher $|\Delta S|_{\text{max}}$ of 15.97 J/(kg K). Therefore, the higher annealing pressure (1 atm) can be helpful to fully exploit the magnetocaloric potential of La(Fe,Si)$_{13}$-based strips.

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I. INTRODUCTION

Magnetic refrigeration is considered to be an alternative refrigeration technology to replace the traditional gas compression--expansion refrigeration technology due to its environmental friendliness and high efficiency.$^{1,2}$ In reality, the magnetic refrigerants used in the magnetic refrigerator are required to have large magnetocaloric effects (MCEs).$^3$ The La(Fe,Si)$_{13}$-based compounds with a cubic NaZn$_{13}$-type structure (1:13 phase), known as one of the most promising magnetic refrigerants, exhibit giant MCEs and have been used in magnetic refrigerator research.$^{4-6}$ However, the 1:13 phase in La(Fe,Si)$_{13}$ compounds is only formed by a peritectoid reaction ($\alpha$-Fe + La-rich phase $\rightarrow$ 1:13 phase) through heat treatment. In addition, a long annealing time of about 7 days is necessary to obtain a high volume fraction of the 1:13 phase in the bulk ingots because of the low atomic diffusivity.$^7$ Although higher annealing temperature can reduce the annealing time,$^8$ it will also result in the coarse graining of the impurity phase $\alpha$-Fe.$^9$ Many new synthetic methods including melt-extraction,$^{10}$ gradient solidification,$^{11}$ and high energy ball-milling$^{12}$ have been proposed. The directionally solidified technique is also reported as another feasible approach to directly obtain a large fraction of the 1:13 phase.$^{13}$ However, the presence of the 1:13 phase in the ingots will separate the $\alpha$-Fe phase away from the La-rich phase, which leads to a fairly long annealing time for the further formation of the 1:13 phase.$^{14}$

Eventually, rapid solidification is found to be one of the most effective technologies to shorten the annealing time for the La(Fe,Si)$_{13}$-based compounds because a homogenized and refined microstructure can be obtained.$^{15-17}$ The annealing time is reduced from a few weeks to several hours.$^{18}$ Liu et al. reported that a high content of 84% of the 1:13 phase was produced in a melt-spun LaFe$_{11.6}$Si$_{14}$ ribbon after a 24-h-long annealing under 40 kPa in a pure Ar atmosphere.$^{19}$ Zhang et al. also reported that after a relatively short annealing time, La(Fe,Mn)$_{11.6}$Si$_{14}$ flakes prepared by strip casting exhibit a nearly single 1:13 phase.$^{20}$
TABLE I. Number of the strips according to different annealing conditions.

| Numbers | Annealing conditions | Surface oxidation | $|\Delta S|_{\text{max}}$ (J kg$^{-1}$ K$^{-1}$) |
|---------|----------------------|-------------------|-------------------------------------|
| Strip 1 | $5 \times 10^{-5}$ Pa for 6 h | No obvious | 12.27 |
| Strip 2 | $5 \times 10^{-5}$ Pa for 48 h | Obvious | 8.14 |
| Strip 3 | $5 \times 10^{-5}$ Pa for 5 days | Very serious | N/A |
| Strip 4 | 1 atm for 48 h | No obvious | 15.97 |
| Strip 5 | Annealing strip 4 at $5 \times 10^{-5}$ Pa for 48 h | Obvious | 4.00 |
| Strip 6 | Annealing strip 4 at 1 atm for 48 h | No obvious | 10.08 |

*aThe maximum magnetic entropy change $|\Delta S|_{\text{max}}$."

On the other hand, it is noteworthy that an oxygen-free environment is required for annealing the La(Fe, Si)$_{13}$ compounds because the La-rich phase is prone to oxidation at a high temperature. The oxidation of bulk LaFe$_{11.5}$Si$_{1.5}C_0.13$ during annealing has been reported previously. The atomic fraction required for the formation of the 1:13 phase is prevented by the oxide barrier. However, for the bulk sample, the oxidation does not have obvious effect on the formation of the 1:13 phase inside the sample. However, few reports focus on the oxidation during the heat treatment of the La(Fe, Si)$_{13}$ strips. After rapid solidification, the strips have a large specific surface area and a very small thickness (usually is less than 1 mm). Therefore, the formation of the 1:13 phase and the magnetocaloric properties of the strips are more sensitive to oxidation during annealing.

In this paper, the role of annealing pressure on the surface oxidation of LaFe$_{11.5}$Si$_{1.5}C_{0.13}$ strips in the heat treatment is explored. The effect of surface oxidation on the formation of the 1:13 phase and the related magnetocaloric properties of the strip during heat treatment are also investigated.

II. MATERIALS AND METHODS

A kilogram-scale ingot with a nominal composition of LaFe$_{11.5}$Si$_{1.5}C_{0.13}$ was synthesized by induction melting. It has been reported that doping carbon will accelerate the formation of the 1:13 phase and reduce the hysteresis loss. In this regard, a small amount of C is added to the sample. The purities of raw materials were 99 wt. % for La and Fe, 99.999 wt. % for Si, and iron-carbon alloy with 5 wt. % C, respectively. The as-cast strips (0.6–0.9 mm in thickness) were prepared by the strip casting on a single copper wheel with diameter $d = 310$ mm. The wheel rotated with a surface speed of 1.2 m/s in vacuum. The casting temperature was above 1753 K.

The surface of the as-cast strips was cleaned by acetone. Then, the strips were sealed in a smaller quartz tube (inner/outer diameter: 12 mm/16 mm). The smaller tube was subsequently sealed into a bigger one (inner/outer diameter: 18 mm/22 mm) to prevent the rupture of the smaller quartz tube during heat treatment. Before the samples were put in the quartz tube, the tubes were heated at 1353 K and then cooled down under vacuum to eliminate the moisture adsorbed on the wall of the quartz tube. The as-cast strips were annealed under pressures both lower and higher than the atmospheric pressure, respectively (dubbed as lower and higher annealing pressure in the following text for clarity). In the case of lower pressure annealing, the inner tube was evacuated and sealed when the pressure reached $5 \times 10^{-5}$ Pa. Regarding the strips annealed under a higher annealing pressure, the inner quartz tube was backfilled with 1 atm high purity Ar after being evacuated to $5 \times 10^{-5}$ Pa at room temperature, then sealed. All of the outer quartz tubes were evacuated to $5 \times 10^{-5}$ Pa, then backfilled with 0.2 atm high purity Ar at room temperature. The strips were annealed at 1353 K for 6 h, 48 h, and 5 days, respectively, and then quenched into ice-cold water. The corresponding strip numbers are listed in Table I.

The room temperature powder x-ray diffraction (XRD) was performed using an x-ray diffractometer with Cu K$_\alpha$ radiation. Microconstituent characterization was carried out by scanning electron microscopy (SEM) with an energy dispersive spectrometry (EDS) attachment. Differential scanning calorimetric (DSC) measurements were carried out to study the thermal effect accompanying the first-order magnetic transitions at a heating rate of 10 K/min. Magnetic properties of the strips were measured by using a Quantum Design VersaLab with a vibrating sample magnetometer (VSM) option. The temperature dependent magnetization ($M$-$T$) curves were measured at a heating and cooling rate of 2 K/min. The isothermal magnetization ($M$-$H$) curve measurements in the vicinity of $T_C$ were carried out under external magnetic fields up to 3 T. The magnetic entropy changes were calculated from $M$-$H$ curves using the Maxwell relations.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for the as-cast and annealed LaFe$_{11.5}$Si$_{1.5}C_{0.13}$ strips. Apart from the α-Fe and LaFeSi, the 1:13 phase is identified from the room temperature powder x-ray diffraction pattern of as-cast strips. The appearance of the 1:13 phase could be due to the rapid solidification. Carbon doping is also reported to be helpful in the formation of the 1:13 phase, facilitating the existence of the 1:13 phase after rapid solidification. Therefore, a high temperature phase (1:13 phase) could be preserved at room temperature. This result is also consistent with the previous literature.

Figure 2(a) displays the photo of a LaFe$_{11.5}$Si$_{1.5}C_{0.13}$ strip in the as-cast state. The strip is shown both in the lateral (left) and thickness (right) directions. It can be observed that the strip is still shiny after rapid solidification, indicating that the surface oxidation does not originate from the preparation of strips. Figure 2(b) shows the back scattered electron (BSE) image of the as-cast LaFe$_{11.5}$Si$_{1.5}C_{0.13}$ strip along the thickness direction. Based on the EDS results, the
dark grey, white, and grey areas denote $\alpha$-Fe, LaFeSi, and 1:13 phases, respectively. The result is consistent with that shown in Fig. 1.

After being annealed with various pressures and times, the strips exhibited different microconstituents. Figure 3 shows the BSE images of annealed LaFe$_{11.5}$Si$_{1.5}$C$_{0.13}$ strips along the thickness direction after different heat treatments. Details of the heat treatments are marked on the images. The composition of the large gray area in Fig. 3 corresponds to the 1:13 phase. The minor dark grey part corresponds to $\alpha$-Fe. In addition, the white part in the gray area corresponds to the La-rich phase. It can be observed from Fig. 3(a) that annealing under lower pressure for 6 h will end up getting a 1:13 phase as the matrix phase with residual $\alpha$-Fe and La-rich phases. Previous reports show that for the arc-melted La(Fe$_{0.89}$Si$_{0.11}$)$_{13}$ (bulk sample), an almost pure 1:13 phase could be obtained by annealing at 1323 K for more than 300 h. In contrast to the long annealing time for bulk alloys, more than 95 vol. % of the 1:13 phase can rapidly form within 48 h by employing the rapid solidification method. The results in this work are also similar to other research on rapid solidification. The reduced annealing time is attributed to the finer grains produced at a higher solidification rate, generating a higher density of phase boundaries that provide efficient diffusion pathways for the elements during annealing. It is worth noting that when the annealing pressure is $5 \times 10^{-5}$ Pa, increasing annealing time was not helpful to eliminate the residual phases but opted to form an oxidized region instead, as shown in Figs. 3(b) and 3(c). On the contrary, Fig. 3(d) shows the BSE images of strip 4, which was annealed for 48 h under higher annealing pressure (1 atm). No obvious oxide layer was observed on the surface of strip 4, and the other impurity phases become much smaller compared with those shown in Fig. 3(b). An almost single 1:13 phase is obtained in strip 4 without surface oxidation.

When the strip is annealed under lower pressure ($5 \times 10^{-5}$ Pa) for 48 h (strip 2), an obvious oxide layer is observed on the surface, as shown in Fig. 3(b). When the strip is annealed for longer, from 48 h to 5 days, the thickness of the oxide layer increases from $\approx 0.08$ mm to $\approx 0.22$ mm. The oxidized region is about more than half of the strip thickness for strip 3, as shown in Fig. 3(c). This is in line with the diffraction peaks observed in Fig. 1. In the case of strip 3, the diffraction peaks of the $\alpha$-Fe phase become higher and the diffraction peaks of the La$_2$O$_3$ phase are also observed in Fig. 1. By comparing the results under different annealing pressures, it can be inferred that it is easier to be oxidized if the strips are annealed under lower annealing pressure during peritectoid reaction. In addition, the oxidation starts from the surface and gradually propagates into the center of a strip as time proceeds. The oxidation of the strips may be related to the residual trace air in the sealed quartz tubes. However, a higher annealing pressure (1 atm) could effectively prevent the strips from oxidation.

The morphologies of the oxide layer of strip 2 and strip 3 are also shown in Fig. 4. Unexpectedly, several Si-rich regions are observed on strips 2 and 3, as shown in Figs. 4(a) and 4(c). The Si-rich regions locate at the interface of the oxide layer and 1:13 phase. The Si-rich regions correspond to the interface of the oxide layer and 1:13 phase. The formation of Si-rich regions could be attributed to the decomposition of the 1:13 phase since these regions could be treated as the transition region from La$_2$O$_3$ + $\alpha$-Fe, as shown in Figs. 4(b) and 4(d), to the La(Fe,Si)$_{13}$ phase. Once the oxidation initiates, oxygen combines with lanthanum; as a consequence, Si from the La-rich phase will diffuse to the area closer to the center. Zooming in to the oxide image in Fig. 4(c) shows the Si-rich region with the transformation of the 1:13 phase. The results obtained in this work are also similar to other research on rapid solidification. The reduced annealing time is attributed to the finer grains produced at a higher solidification rate, generating a higher density of phase boundaries that provide efficient diffusion pathways for the elements during annealing. It is worth noting that when the annealing pressure is $5 \times 10^{-5}$ Pa, increasing annealing time was not helpful to eliminate the residual phases but opted to form an oxidized region instead, as shown in Figs. 3(b) and 3(c). On the contrary, Fig. 3(d) shows the BSE images of strip 4, which was annealed for 48 h under higher annealing pressure (1 atm). No obvious oxide layer was observed on the surface of strip 4, and the other impurity phases become much smaller compared with those shown in Fig. 3(b). An almost single 1:13 phase is obtained in strip 4 without surface oxidation.

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layer, as shown in Figs. 4(b) and 4(d), it mainly consists of black and white lamellae. According to EDS, the white and black areas in the lamellae correspond to \( \text{La}_2\text{O}_3 \) and \( \alpha\text{-Fe} \) (with \( \sim 10 \text{ at. \% Si} \)), respectively. The microstructure of the oxide lamellae is in accord with the results from the literature. It is noticed that the oxide layer is composed of coarse and fine lamellae, and the distribution of these two lamellae is irregular.

Linear scanning analysis was carried out along the thickness direction of strips 2 and 3, and the results are shown in Fig. 5. The oxygen content increases abruptly to 5–15 at. % with the position approaching the strip surface, as shown in Fig. 5. It indicates that the oxidation starts from the surface if the strips were annealed under lower annealing pressure. In addition, the Si content in the oxidized region is below the average Si content on the strip. However, the Si content on the boundary of the oxide layer/1:13 phase is found to be above the average and then regress to the average value when the position moves toward the center. It is concluded that due to the oxidation, the distribution of elements in the 1:13 phase becomes nonuniform on the same strip. These are good pieces of evidence to support the conclusions drawn from Figs. 4(a) and 4(c). The oxidation will cause the formation of \( \text{La}_2\text{O}_3 \) and \( \alpha\text{-Fe (Si)} \) and part of the Si will diffuse to the regions closer to the center. The inhomogeneous composition of the 1:13 phase could lead to the detrimental effects on the magnetocaloric properties of those strips, which will be discussed later.

In order to further study the surface oxidation of \( \text{LaFe}_{11.5}\text{Si}_{1.5}\text{C}_{0.13} \) strips during the heat treatment, an additional heat treatment was carried out on the annealed strips. The annealed strip...
4 composed almost entirely of the 1:13 phase was chosen to be re-annealed under different pressures for another 48 h. Strip 5 and strip 6 are obtained from the re-annealing of strip 4, as shown in Table 1. The BSE images and linear scanning data of strip 5 and strip 6 are displayed in Fig. 6. After re-annealing under lower pressure ($5 \times 10^{-5}$ Pa), an obvious oxide layer appears on the surface of strip 5. This suggests that the 1:13 phase on the surface decomposes due to oxidation.
Comparing the BSE images of strip 5 with those of strip 2 [Fig. 4(b)], it can be found that the morphology of oxide layers in strip 5 is different from that in strip 2, which was oxidized during the heat treatment of the as-cast strip. The lamellae oxide of strip 2 is uneven and irregular. However, when strip 4 composed almost entirely of the 1:13 phase was re-annealed, the oxide layer shows good regularity, as shown in the enlarged image of Fig. 6(a). The oxide layer in strip 5 consists of coarse lamellae La$_2$O$_3$/α-Fe and finer lamellae La$_2$O$_3$/α-Fe. The finer lamellae La$_2$O$_3$/α-Fe are close to the interior of the strips and away from the surface, while coarse lamellae La$_2$O$_3$/α-Fe are on the surface. It is presumed that the 1:13 phase on the surface of a strip was decomposed by oxidation preferentially by heat treatment. Then, the grain size of α-Fe and La oxides on the surface grew up as the annealing runs. Therefore, the morphology of oxide layers in strip 2 shows no regularity.

Regarding strip 6 re-annealed under a higher annealing pressure of 1 atm, a thin (∼0.03 mm) oxide layer is observed on the surface of the strip, as shown in Fig. 6(b). By comparing the linear scanning data in Figs. 6(c) and 6(d), it can be seen that the surface oxidation of the strips re-annealed under two kinds of annealing pressures are obviously different. After being re-annealed under higher pressure, the thickness of the oxide layer of strip 6 is smaller than that of strip 5, and the Si content on the boundary of the oxide layer/1:13 phase does not change significantly. The results show that compared with strip 6, the surface of strip 5 is seriously oxidized. This also indicates that the higher annealing pressure could inhibit the 1:13 phase from severe oxidation and decomposition.

As shown above, the annealing pressure could have pronounced impacts on the formation and oxidation of the 1:13 phase. The influences were further characterized on behalf of magnetocaloric effects. The magnetic transition temperature ($T_C$) of the strips was examined by DSC. Three samples were randomly selected from the strips with the same heat treatment to characterize the uniformity of the strips. Figure 7 shows the DSC heating curves of the LaFe$_{11.5}$Si$_{1.5}$C$_{0.13}$ strips, where the Roman numbers in Fig. 7 serve to denote different samples with the same heat treatment. The $T_C$ corresponds to the endothermal peak of the DSC curve. For strip 1, $T_C$’s of the samples are consistent. These results suggest that the composition of the 1:13 phase be homogeneous on strip 1 because $T_C$ is very sensitive to the composition of the magnetic materials. $T_C$ of strip 1 is about 215 K. When the annealing time was prolonged to 48 h under lower annealing pressure (5 × 10$^{-3}$ Pa), the endothermal peaks for the three samples from strip 2 do not coincide but get broadened. Two peaks located at ∼218 K and ∼221 K can be vaguely observed, signifying the phase separation in the strip. Combining with the SEM images for strip 2, the change could be due to the serious oxidation on the surface, which leads to the decrease in the effective amount of the 1:13 phase and the inhomogeneous composition of the 1:13 phase. However, after annealing under a higher annealing pressure of 1 atm for 48 h, the $T_C$’s of the samples from strip 4 are the same, which is 215 K.

It indicates that there is no obvious change in the composition of the 1:13 phase. In addition, the endothermal peak in the curves of strip 4 is much narrower. It means that strip 4 exhibits a more abrupt phase transition. These pieces of evidence suggest that the oxidation of the strips obviously affects the first order magnetic transition temperature $T_C$. A higher annealing pressure can help to obtain consistent $T_C$ on the strip.

The temperature-dependent magnetization ($M$-$T$) curves of the LaFe$_{11.5}$Si$_{1.5}$C$_{0.13}$ strip annealed under different conditions are measured in a low magnetic field of 0.01 T, as shown in Fig. 8(a). It is noticed that for strip 2 and strip 5, the magnetization above $T_C$ did not drop to zero. It means the existence of the α-Fe phase because $T_C$ of α-Fe is at a much higher temperature. Surface oxidation for strip 2 and strip 5 would lead to an increase in the amounts of α-Fe. Besides, the $M$-$T$ curves of strip 2 and strip 5 become gradual around $T_C$, which suggests inhomogeneity on these strips. The $M$-$T$ curves of strip 1 are similar to those of strip 4, but there is still a small magnetization above $T_C$. It indicates that α-Fe existed in strip 1, which is due to the incomplete peritectoid reaction after a six-hour-long heat treatment.

Figure 8(b) shows the temperature dependence of the magnetic entropy change for annealed LaFe$_{11.5}$Si$_{1.5}$C$_{0.13}$ strips. The maximum magnetic entropy changes $|\Delta S|_{\text{max}}$ for those strips are given in Table 1. Because of the oxidation, strip 2 and strip 5 exhibit much smaller values of $|\Delta S|_{\text{max}}$. On the contrary, after annealed under higher annealing pressure, strip 4 shows larger $|\Delta S|_{\text{max}}$ [15.97 J/(kg K)]. The larger value of $|\Delta S|_{\text{max}}$ is due to the fact that strip 4 is not oxidized during heat treatment and the composition of the 1:13 phase is homogeneous in strip 4. As shown above, there is
a close relationship between the annealing pressure and magnetism. Although all the strips were evacuated to $5 \times 10^{-5}$ Pa before annealing, the higher annealing pressure can impede the oxidation process and improve magnetocaloric properties during the heat treatment.

IV. CONCLUSIONS

In summary, a lower annealing pressure ($5 \times 10^{-5}$ Pa) will lead to obvious oxidation on the surface of the LaFe$_{11.5}$Si$_{1-x}$Co$_{13}$ strip during heat treatment. As a result, the chemical composition of the 1:13 phase becomes nonuniform on the strips. By re-annealing the strips with almost a single 1:13 phase, the oxidation caused by the lower annealing pressure also leads to the decomposition of the 1:13 phase during the heat treatment. When the strip with an almost pure 1:13 phase is re-annealed, the oxide layers formed are even and consist of regular lamellae. In contrast, the oxide layers are irregular when the as-cast strips are annealed. However, the strips do not exhibit an oxide layer after being annealed under a higher pressure (1 atm). Because of the oxidation, the $\Delta S_{\text{max}}$ of the strips gets drastically reduced from 12.27 J/(kg K) to 4.00 J/(kg K). Therefore, increasing the annealing pressure during the heat treatment can effectively protect the strip from surface oxidation. Additionally, strips without surface oxidation will show larger magnetocaloric effects compared with those with oxidation.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (Grant Nos. 51571018 and 51371026), the National Key Research and Development Program of China (Grant No. 2017YFB0702704), and the Scientific and Technological Innovation Team Program of Foshan (Grant No. 2015IT100044).

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FIG. 8. (a) M–T curves for LaFe$_{11.5}$Si$_{1-x}$Co$_{13}$ strips under different annealing conditions. (b) Magnetic entropy changes of annealed LaFe$_{11.5}$Si$_{1-x}$Co$_{13}$ strips under 0–2 T field change.
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