Rare Metal Materials and Engineering
Volume 51, Issue 4, April 2022
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Fu Xiaokun, Shu Rong, Hou Yuhua, et al. Microstructure and Magnetocaloric Effect of Spark Plasma Sintered LaFeSi Magnets with LaAl Addition[J]. Rare Metal Materials and Engineering, 2022, 51 (04): 1239-1244.

ARTICLE

Microstructure and Magnetocaloric Effect of Spark Plasma Sintered LaFeSi Magnets with LaAl Addition

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Abstract: Using $LaFe_{11.3}Si_{1.7}$ and $La_{0.77}Al_{0.23}$ alloys as precursors, the bulk LaFeSi samples with excellent magnetocaloric performance were synthesized through the spark plasma sintering (SPS) technology. The results show that the $La_{0.77}Al_{0.23}$ compound with a low melting point is helpful in facilitating peritectic reaction, and $NaZn_{13}$-type phase with high content can be achieved. A slight itinerant-electron-metamagnetic transition is observed. The increased thermal annealing time facilitates magnetic transition from the first order to the second order, which is ascribed to the excessive Al diffusion into the 1:13 phase. Under the thermal treatment condition of 1000 °C/6 h, the maximum entropy change $(-\Delta S_M)^{max}$ of 12.40 J·kg^{-1}·K^{-1} can be obtained, and the highest refrigerating capacity, up to 318.40 J·kg^{-1}, is achieved under thermal annealing condition of 1000 °C/10 h.

Key words: LaFeSi; magnetocaloric effect; microstructure

Giant magnetocaloric effect materials are widely concerned for their energy conservation and high efficiency, and are potential candidates for gas compression refrigeration materials[1-5]. Several families of magnetocaloric materials have been found such as Mn-based alloys with Fe_2P-type structure[6], $Gd_5(Si_xGe_{1-x})_4$[7] and $LaFe_{13-x}Si_x$ with 1:13 phase[8-10], among which the LaFeSi-based alloys have the advantages of low cost, non-toxicity, giant magnetocaloric effect and tunable operating temperature, which has been widely concerned[3,11-14]. Generally, when $1.0 \le x \le 1.6$, the $LaFe_{13-x}Si_x$ compounds demonstrate the characteristics of first order transition, and excellent magnetocaloric performance can be obtained, accompanied by itinerant-electron-metamagnetic transformation from paramagnetism to ferromagnetism and the large change of cell volume approaching T_C[15-18]. However, due to the large thermal hysteresis loss and narrow operating temperature scope, the application of first order materials is greatly limited. For $x>1.6$[19,20], LaFeSi materials generally exhibit almost no magnetic and thermal hysteresis loss, and possess wide operating temperature scope, thus showing great potential application, although having the disadvantage of smaller magnetic entropy change. In the previous study, through adding LaAl alloy during sintering, LaFeSi samples with first order transition were prepared, and it is found that the peritectic reaction can be facilitated, and meanwhile the densification of samples is also improved significantly[21]. In this work, based on the SPS technique, LaFeSi magnets with second order transition were synthesized, and microstructure evolution and magnetocaloric performance optimization were studied.

1 Experiment

$La_{0.77}Al_{0.23}$ and $LaFe_{11.3}Si_{1.7}$ alloys were fabricated through arc melting followed by melt spinning in the argon atmosphere with high purity, under the optimal speed of 35 m/s. The purity of initial materials for Fe, Si, La and Al was 99.95wt%, 99.9wt%, 99.5wt% and 99.996wt%, respectively. Additional 5wt% of La was appended to compensate the La loss during arc melting. The mass ratio of blended powders for $LaFe_{11.3}Si_{1.7}$ and $La_{0.77}Al_{0.23}$ was 0.95: 0.05 according to the

Received date: April 21, 2021
Foundation item: National Natural Science Foundation of China (51961027, 51564037, 51401103); Key Research and Development Program of Jiangxi Province (20181ACE50005, 20192ACB50020); Postgraduate Innovation Special Fund of Jiangxi Province (YC2019005)
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optimized processes[21]. Using the optimized process parameter (1000 °C/50 MPa/10 min), the bulk samples were prepared by SPS. Afterwards, magnetocaloric performance was adjusted by thermal annealing at 1000 °C for 6~12 h, in an evacuated quartz tube cleaned by argon, followed by water quenching. For comparison, the $La_{0.77}Al_{0.23}$-free sintered samples were also prepared, and the optimized thermal annealing process was determined (1000 °C/10 h). The microstructural morphology of samples was characterized through a QUANTA-200 scanning electron microscope. The compositional constituent was determined using the energy dispersive spectrometer (EDS). Magnetic performance was tested by a PPMS-DynaCool system in the temperature interval from 50~380 K with a maximum 5 T magnetic field.

2 Results and Discussion

XRD patterns of $LaFe_{11.3}Si_{1.7}/La_{0.77}Al_{0.23}$ samples annealed at 1000 °C for 6~12 h are demonstrated in Fig. 1, and for comparison, XRD pattern of $La_{0.77}Al_{0.23}$-free sintered $LaFe_{11.3}Si_{1.7}$ sample annealed at 1000 °C for 10 h is also supplied. One can see from Fig. 1 that sintered samples all contain 1:13 phase and α-Fe phase, whether or not $La_{0.77}Al_{0.23}$ alloy is added. For sintered samples with and without $La_{0.77}Al_{0.23}$ addition, it is found that in comparison with the diffraction peak intensity of 1:13 phase, that of residual α-Fe phase reduces significantly, indicating that the added $La_{0.77}Al_{0.23}$ alloy is helpful in elevating the content of 1:13 phase, which is due to the fact that the introduction of La element from $La_{0.77}Al_{0.23}$ is helpful in facilitating the peritectic reaction[2]. For LaFeSi/$La_{0.77}Al_{0.23}$ samples, when annealing was at 1000 °C for 6 h, compared to the intensity for α-Fe phase diffraction peak, the maximum peak intensity of 1:13 phase can be observed among samples, indicating that the maximum content of $NaZn_{13}$-type phase has been achieved. However, upon increasing thermal treatment time to 10 h, in comparison with the diffraction peak intensity of 1:13 phase, that of the α-Fe phase increases significantly. With enhancing thermal annealing time to 12 h, the diffraction peak corresponding to the 1:1:1 phase can be observed, indicating that the 1:13 phase may have been decomposed[21].

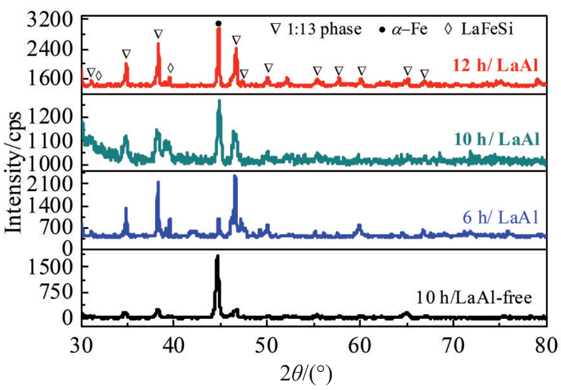

Fig.1 XRD patterns of $LaFe_{11.3}Si_{1.7}$ samples with and without LaAl addition annealed at 1000 °C for 6, 10 and 12 h

SEM image of sintered $LaFe_{11.3}Si_{1.7}$ sample is illustrated in Fig. 2a. One can see that there are three zones with various contrasts, i. e. grey zone, black zone and white zone, represented by point 1, 2, and 3, respectively. From EDS results listed in Table 1, it can be seen that for the point 1 in gray zone, the elemental composition of La, Fe and Si is 7.66at%, 78.46at%, and 13.89at%, respectively, indicating that the gray zone should be 1:13 phase. As to the black zone, the Fe content of 88.55at% is determined, meaning that it is α-Fe phase. For point 3, the elemental composition consists of

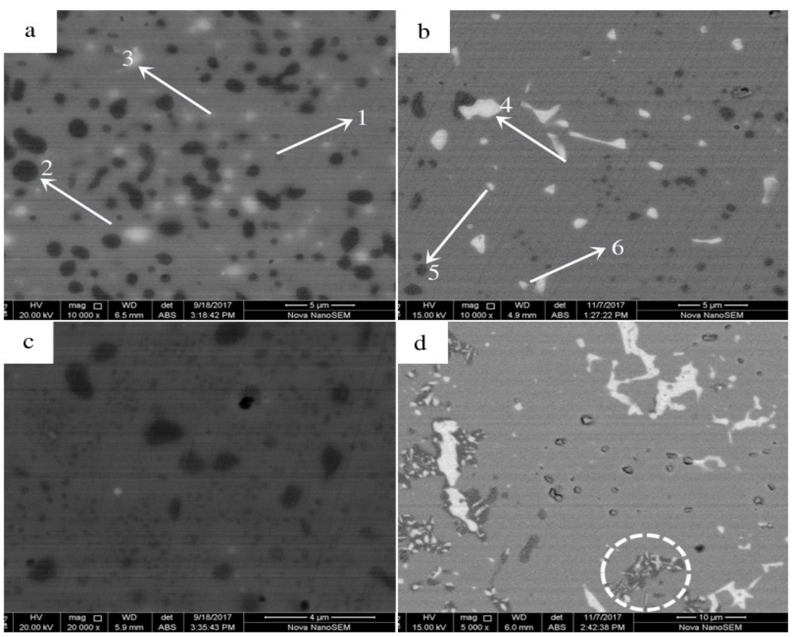

Fig.2 Microstructural morphologies of $LaFe_{11.3}Si_{1.7}$ samples without (a) and with (b~d) LaAl addition annealed at 1000 °C for different time: (a) 10 h, (b) 6 h, (c) 10 h and (d) 12 h

60.61at% La, 31.45at% Fe and 7.49at% Si, demonstrating the La-rich phase. The microstructure of $LaFe_{11.3}Si_{1.7}/La_{0.77}Al_{0.23}$ samples are displayed in Fig. 2b~2d. It is found that equally sintered LaFeSi samples with $La_{0.77}Al_{0.23}$ addition are also composed of three zones with the same contrast, as represented by point 4, 5 and 6 in Fig.2b, i.e. La-rich phase, α-Fe phase and 1:13 phase, respectively. The difference is that the Al element can all be observed in three different zones as demonstrated in Table 1, which ascribes to the addition of $La_{0.77}Al_{0.23}$ in sintering, suggesting that the Al element has diffused into La-rich phase, α-Fe phase and 1: 13 phase. Comparing Fig. 2a with Fig. 2c, it is shown that the surface fraction of black zone decreases from 13.1% to 5.7%, indicating that the addition of $La_{0.77}Al_{0.23}$ intergranular phase can reduce the α-Fe phase content in sintered samples. The introduction of La element to the promotion of peritectic reaction should be responsible for this[2]. This is also in accordance with the discussion of XRD in Fig.1.

The thermal treatment processes have an important influence on magnetocaloric performance and microstructure. When annealing is at 1000 °C for 6 h, La-rich phase, 1:13 phase and a little of α-Fe phase can be found in $LaFe_{11.3}Si_{1.7}/La_{0.77}Al_{0.23}$ sample. When the annealing time of 10 h is adopted, the surface fraction of black zone increases from 0.9% to 5.7%, indicating the rise of α-Fe phase content. Prolonging the annealing time to 12 h, a large number of white zones consisting of La-rich phase (the volume fractions of around 7.1%) are formed, and some lamellar microstructures are also observed, as shown in dotted line circles in Fig. 2d, generally signifying the decomposition of 1:13 phase[10].

Fig. 3 shows the magnetization (M) vs temperature (T) curves for sintered $LaFe_{11.3}Si_{1.7}$ sample annealed at 1000 °C for 10 h and $LaFe_{11.3}Si_{1.7}/La_{0.77}Al_{0.23}$ samples annealed at 1000 °C for 6, 10, and 12 h, under 4×10^4 A/m magnetic field over a temperature range of 50~380 K. It can be seen that compared with $La_{0.77}Al_{0.23}$-free $LaFe_{11.3}Si_{1.7}$ magnet, the lower residual magnetization is observed in the case of paramagnetism above T_C for $LaFe_{11.3}Si_{1.7}/La_{0.77}Al_{0.23}$ samples, meaning that the addition of $La_{0.77}Al_{0.23}$ is helpful in reducing α-Fe phase content, which is also in agreement with the previous discussion of XRD patterns and SEM images. Meanwhile, it is found that $LaFe_{11.3}Si_{1.7}/La_{0.77}Al_{0.23}$ magnet annealed for 6 h possesses the minimum value of residual magnetization above Curie temperature and the steepest transition from ferromagnetism to paramagnetism, which suggests that 1:13 phase of the highest content can be obtained, and excellent magnetocaloric performance will be achieved. Upon increasing annealing time to 12 h, the higher residual magnetization in the paramagnetic state indicates that much more α-Fe phase will exist in comparison with samples produced for 6 and 10 h.

Table 1 EDS results for different zones represented by points 1, 2, 3, 4, 5 and 6 in Fig.2a and Fig.2b (at%)

Point	Al	La	Fe	Si
1	-	7.66	78.46	13.89
2	-	4.16	88.55	7.28
3	-	60.61	31.45	7.94
4	1.25	40.99	53.16	4.60
5	1.76	0.33	90.41	7.50
6	4.33	7.69	74.23	13.75

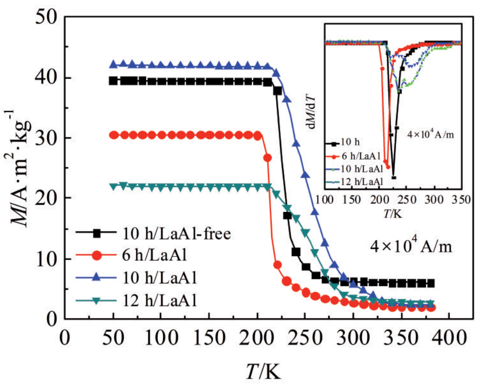

Fig.3 Magnetization (M) vs temperature (T) curves for $LaFe_{11.3}Si_{1.7}$ samples with and without $La_{0.77}Al_{0.23}$ addition annealed at 1000 °C for 6, 10 and 12 h

Fig. 4 displays isothermal magnetization curves for $LaFe_{11.3}Si_{1.7}$ samples with and without $La_{0.77}Al_{0.23}$ addition. For all the samples, upon measured temperature is lower than the respective T_C, the saturation magnetization is reached rapidly in a small magnetic field, showing a ferromagnetic characterization. While the tested temperature is higher than the corresponding T_C, the samples demonstrate the paramagnetic character. During this transition of FM-PM process, a slight itinerant-electron-metamagnetic transition and magnetic hysteresis can be observed in Fig. 4b, which is attributed to the high Si content of initial compositional design[19, 20].

Arrott curves can be determined according to Laudau theory. Generally, the first order transition presents S-shape characteristics in Arrot curves, and the linear relationship above Curie temperature implies the second order magnetic transition. Arrott curves of sintered samples with and without $La_{0.77}Al_{0.23}$ addition are displayed in Fig. 5. It is seen that the $La_{0.77}Al_{0.23}$-free magnet shows the characteristics of the second order transition, caused by the initial compositional design. However, in the sintered $LaFe_{11.3}Si_{1.7}/La_{0.77}Al_{0.23}$ sample annealed for 6 h, the weak S-type characteristics in Arrott curves are observed, demonstrating the first order magnetic transition characteristics, which is attributed to the diffusion of La into 1: 13 phase. Meanwhile, with the increase of annealing time, the characteristics of S-shape for Arrott curves vanish, showing the linear relationship above T_C. It means that a magnetic behavior changes from the first toward the second order, which should be attributed to the excessive Al diffusion into 1:13 phase [21].

Based on the Maxwell relation, the magnetic entropy change ΔS_M can be determined. Fig.6 shows $(-\Delta S_M)$-T curves

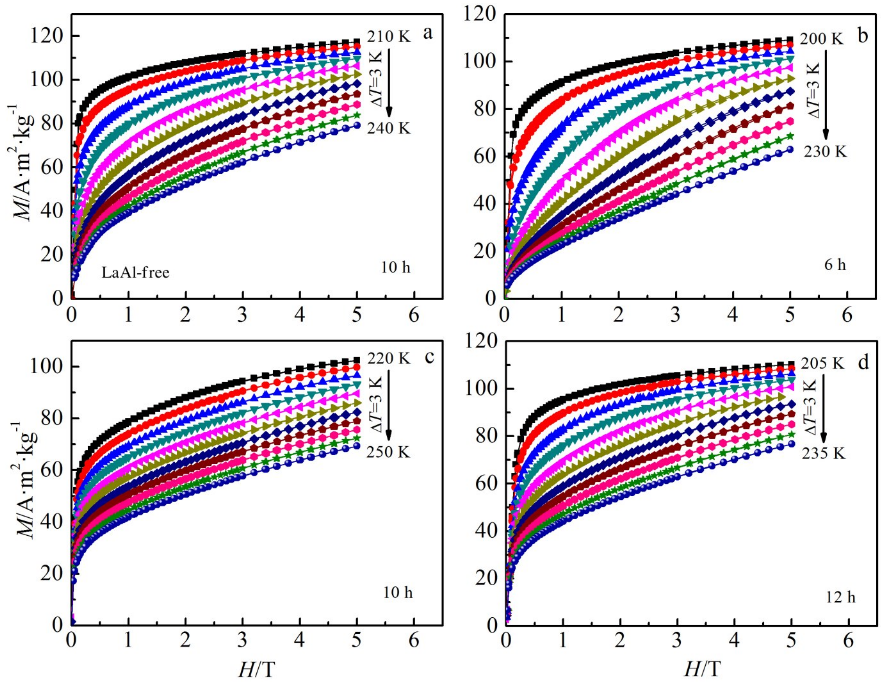

Fig.4 Isothermal magnetization curves of $LaFe_{11.3}Si_{1.7}$ samples without $La_{0.77}Al_{0.23}$ (a) and with 5wt% $La_{0.77}Al_{0.23}$ (b~d) annealed at 1000 °C for 6, 10 and 12 h

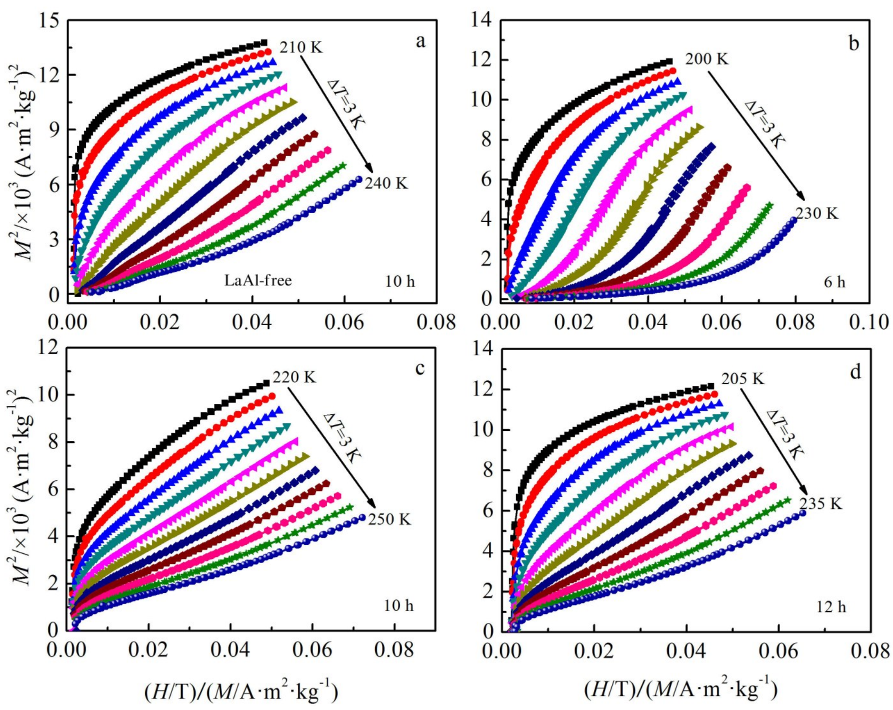

Fig.5 Arrott curves of $LaFe_{11.3}Si_{1.7}$ samples without (a) and with (b~d) $La_{0.77}Al_{0.23}$ annealed at 1000 °C for 6, 10 and 12 h

for $LaFe_{11.3}Si_{1.7}$ samples without and with $La_{0.77}Al_{0.23}$ addition under different annealing time, within a 0~5 T magnetic field range. Refrigeration properties, Curie temperature and thermal hysteresis are shown in Table 2. As for sintered magnet without $La_{0.77}Al_{0.23}$ addition, the highest value of 10.26 $J\cdot kg^{-1}\cdot K^{-1}$ for $(-\Delta S_M)^{max}$ can be obtained. Through adding $La_{0.77}Al_{0.23}$ alloy during sintering, the highest $(-\Delta S_M)^{max}$ value of 12.40 $J\cdot kg^{-1}\cdot K^{-1}$ is achieved, which suggests that the added $La_{0.77}Al_{0.23}$ alloy is helpful in elevating magnetocaloric performance. For $LaFe_{11.3}Si_{1.7}/La_{0.77}Al_{0.23}$ samples, upon raising the annealing

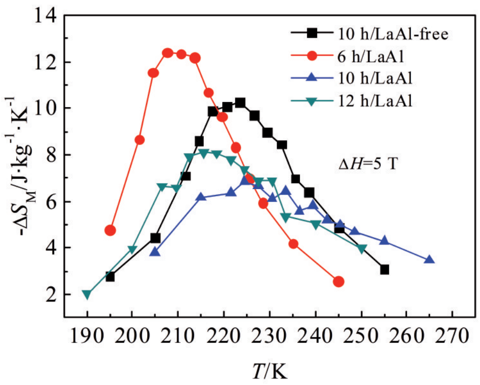

Fig.6 $-\Delta S_M$ vs T curves of $LaFe_{11.3}Si_{1.7}$ samples without $La_{0.77}Al_{0.23}$ and with 5wt% $La_{0.77}Al_{0.23}$ annealed at 1000 °C for different time within the field range of 0~5 T

Table 2 Curie temperature, thermal hysteresis, and refrigeration properties for the $La_{0.77}Al_{0.23}$-free magnet and LaAl added $LaFe_{11.3}Si_{1.7}$ samples annealed at 1000 °C for various time

Sample	T_C/K	Thermal hysteresis/K	$(\Delta S_M)^{max}$/ J·kg^{-1}·K^{-1}	RC/J·kg^{-1}
10 h/LaAl-free	225	10	10.26	299.50
6 h/LaAl	215	15	12.40	299.83
10 h/LaAl	235	10	6.85	318.40
12 h/LaAl	220	5	8.12	306.69

time, the obtained low maximum magnetic entropy change may be attributed to the dissolution of excess Al in 1: 13 phase. However, the maximum refrigeration capacity (RC) of 318.40 J·kg^{-1} is found in the sample annealed for 10 h, which is ascribed to its low thermal hysteresis. Curie temperature T_C of LaFeSi samples can be determined according to the inset in Fig.3, as listed in Table 2, and it changes between 215 and 235 K. As analyzed above, Al element has dissolved into $NaZn_{13}$-type phase to replace the Fe. As a result, the antiferromagnetic interaction between Fe-Al atoms is enhanced, and meanwhile, the elevated volume of unit cell aroused by Al replacing Fe can increase exchange coupling between Fe-Fe atoms. Therefore, the variation of Curie temperature between 215~222 K should be ascribed to this.

3 Conclusions

1) Through adding $La_{0.77}Al_{0.23}$ alloy during sintering, the bulk $LaFe_{11.3}Si_{1.7}/La_{0.77}Al_{0.23}$ samples can be prepared by SPS technology.

2) The addition of $La_{0.77}Al_{0.23}$ is facilitated to the rise of 1:13 phase content, and can suppress the formation of α-Fe phase, which is due to the fact that the introduction of La element from $La_{0.77}Al_{0.23}$ is helpful in promoting peritectic reaction.

3) The thermal treatment processes have an important influence on the magnetocaloric effect and microstructure. A tendency of magnetic transformation from the first order toward the second order can be induced by prolonging annealing time. The highest $(-\Delta S_M)^{max}$, up to 12.40 J·kg^{-1}·K^{-1}, and the maximum refrigeration capacity of 318.40 J·kg^{-1} can be achieved when thermal treatment time is 6 and 10 h, respectively. Meanwhile, a slight magnetic hysteresis loss and itinerant-electron-metamagnetic phenomenon can be observed.

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LaAl添加对放电等离子烧结LaFeSi磁体微观结构和磁热效应的影响

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摘　要：使用$LaFe_{11.3}Si_{1.7}$薄带合金为前驱体粉末，研究了低熔点$La_{0.77}Al_{0.23}$合金添加对放电等离子烧结磁体微观结构和磁热性能的影响。研究发现，适量低熔点LaAl合金的添加能够促进包晶反应，制得了具有较高1:13相含量的LaFeSi磁体。磁体中观察到有微弱的巡游电子变磁转变现象的存在。热处理工艺研究显示，退火时间的增加会使得磁体的磁性转变由一级向二级变化，这主要归因于Al向1:13相内部的扩散。1000 ℃/6 h热处理工艺条件下，其在0~5 T磁场变化下的磁熵变最大，达12.40 $J\cdot kg^{-1}\cdot K^{-1}$，而1000 ℃/10 h条件下所获得磁体的制冷能力最强，为318.40 $J\cdot kg^{-1}$。

关键词：LaFeSi；磁热效应；微观结构

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