

Effect of Ce, Co, B on formation of LaCo_{13} -structure phase in $\text{La}(\text{Fe}, \text{Si})_{13}$ alloys

Xiang CHEN^{1,2}, Yun-gui CHEN¹, Yong-bai TANG¹, Ding-quan XIAO¹

1. School of Materials Science and Engineering, Sichuan University, Chengdu 610065, China;

2. College of Engineering and Technology, Neijiang Normal University, Neijiang 641002, China

Received 2 February 2013; accepted 5 November 2013

Abstract: The effect of Ce, Co, and B on the formation of 1:13 phase in $\text{La}(\text{Fe}, \text{Si})_{13}$ alloys was investigated by XRD, SEM and EDS. The results show that Co can improve the formation of 1:13 phase in as-cast $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ alloys, but in as-cast and annealed $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ alloys, it will hamper the formation of 1:13 phase and help the formation of α -Fe(Co, Si) solid solution. $\text{Ce}_2\text{Fe}_{17}$ phases will form when x reaches a certain value in as-cast and annealed $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ alloys. B can improve the formation of 1:13 phase accompanied with Fe_2B phase in as-cast $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ alloys. B improves the formation of α -Fe solid solution in $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$ alloys, and there is almost only α -Fe in as-cast and annealed $\text{LaFe}_{11.6}\text{Si}_{0.9}\text{B}_{0.5}$ alloy. In all, the introduction of Co, B, and Ce cannot eliminate the α -Fe phases in corresponding alloys prepared by the high-temperature and short-time annealing process.

Key words: $\text{LaFe}_{13-x}\text{Si}_x$ alloys; high-temperature and short-time annealing; 1:13 phase

1 Introduction

The $\text{LaFe}_{13-x}\text{Si}_x$ alloys with $1.1 \leq x \leq 1.6$ have several advantages in comparison with the other magnetic refrigeration materials with giant magnetocaloric, such as the low price of starting materials and excluding deleterious elements, which have been investigated extensively [1–4]. In $\text{LaFe}_{13-x}\text{Si}_x$ alloys, Si element is very important to form and stabilize LaCo_{13} -type phase, lower the content of Si, and prolong the annealing time. In fact, the binary LaFe_{13} alloy does not exist due to a positive formation heat between La and Fe. In hypothetical LaFe_{13} alloy, the Fe atoms would be located at two different crystal sites: Fe I at the Wyckoff position 8b (0, 0, 0) and Fe II at 96i (0, y , z) in a ratio of 1:12. The La atoms are located at 8a (1/4, 1/4, 1/4) surrounded by 24 Fe II atoms, and one central Fe I atom and its nearest neighbors of 12 Fe II atoms form a cluster. In the LaCo_{13} -type $\text{LaFe}_{13-x}\text{Si}_x$ alloys, Si atoms in $\text{LaFe}_{13-x}\text{Si}_x$ randomly occupy both 8b and 96i sites [5]. The substitution of elements with similar chemical properties is the common way of improving comprehensive properties of materials. Ce substituting La in $\text{La}_{1-y}\text{Ce}_y\text{Fe}_{13-x}\text{Si}_x$ alloys has been investigated

extensively [6–9]. The reason is that the single LaCo_{13} -type structure can be obtained when the $\text{CeFe}_{13-x}\text{Si}_x$ ($2.4 \leq x \leq 2.6$) alloys are annealed only for 12 h [10]. For Fe element, most researches are on the Co substitution [11–14]. The reason may be that LaCo_{13} with $T_c = 1297$ K is the only stable alloy among the RT_{13} alloys (R =rare earth elements, T =transition elements) [15]. The result shows that the preferential substitution of Co atoms at Fe II 96i site effectively lowers the La–Fe positive formation heat to stabilize the cubic LaCo_{13} -type structure in $\text{La}(\text{Fe}, \text{Co})_{13-x}\text{Si}_x$ alloys [16]. Besides the $\text{LaFe}_{11.7}\text{Si}_{1.3-x}\text{Cu}_x$ alloys [17], the investigations on the nominal substitution for Si were rarely reported. As grain refining agents in steel, boron atoms are also introduced in the form of interstitial atoms in $\text{LaFe}_{13-x}\text{Si}_x\text{B}_y$ alloys. Addition of boron improves formation of the LaCo_{13} -type phase in as-cast $\text{LaFe}_{13-x}\text{Si}_x$ alloys [18]. In addition, the result of the introduction of B as the substitution element for Fe or Si in $\text{LaFe}_{13-x}\text{Si}_x$ alloys shows that all the annealed samples exhibited a cubic LaCo_{13} -type structure with a few percent of α -Fe and La-rich phases in $\text{LaFe}_{11.9}\text{Si}_{1.1}$, $\text{LaFe}_{11.5}\text{B}_{0.4}\text{Si}_{1.1}$, and $\text{LaFe}_{11.0}\text{B}_{0.5}\text{Si}_{1.5}$ samples [19]. Up to now, the studies about the introduction of Ce, Co, B in $\text{LaFe}_{13-x}\text{Si}_x$ alloys have been focused on the influence of magnetocaloric

properties. However, there are few elaborate studies on the effects of the substitution of Ce and Co for La and Fe, respectively, also the introduction of B as interstitial or substitutional atoms on the formation of LaCo_{13} -structure phase in as-cast and annealed $\text{LaFe}_{13-x}\text{Si}_x$ alloys have not been studied yet.

In this work, the phase and microstructure of the as-cast and annealed $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$, $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$, $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$, $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$, and $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$ alloys are investigated. In addition, based on the random distribution of Si atoms on both of Fe sites in LaCo_{13} -type $\text{LaFe}_{13-x}\text{Si}_x$ alloys, the effects of Co and B on the formation of LaCo_{13} -structure phase in $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$, $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ and $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$ alloys are investigated.

2 Experimental

Approximately 10 g polycrystalline $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$, $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$, $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$, $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$, $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$, $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$ buttons were fabricated, respectively by conventional arc melting in a high purity argon atmosphere using high purity (La 99.4%, Ce 99.9%, Fe 99.9%, Si 99.9999%, Co 99.9%, B 99.9%) elements after the alloys were re-melted five times to achieve a homogeneous composition. The as-cast alloys were divided into two parts. One part was annealed by different high-temperature and short-time processes in a molybdenum wire furnace of 3×10^{-3} Pa, followed by furnace cooling down to room temperature. The phase purity and crystal structure were determined by powder X-ray diffraction (XRD) using Cu (K_α) radiation (Dandong DX-2600). Scanning electron microscopy (SEM) and energy disperse spectroscopy (EDS) observation were carried out with Hitachi S-3400N.

3 Results and discussion

Figure 1 shows the XRD patterns of as-cast $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ and $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ alloys. By analyzing and indexing the X-ray diffraction patterns, it can be found that the as-cast $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ alloys mainly consist of α -Fe and LaFeSi phases. As non-equilibrium solidification phase, a certain amount of 1:13 phase is also observed, but the amount of 1:13 phase is different in the as-cast alloys. The diffraction intensity ratio of 1:13 phase has no obvious change with $x=0.0, 0.3$ and 0.5 , but there is a sharp increase when $x=0.7$ in as-cast $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ alloys. This indicates that Co can improve 1:13 phase in as-cast $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ alloys only when Co reaches a certain amount.

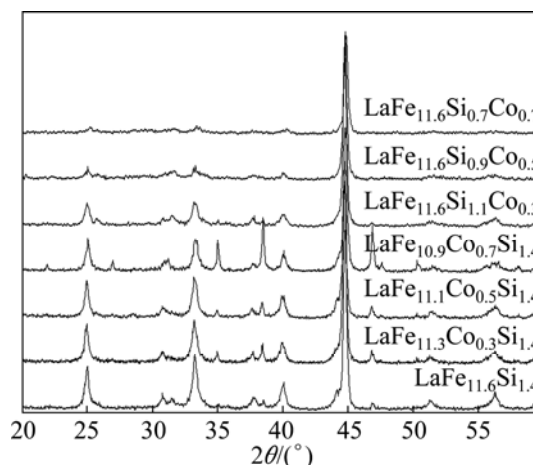


Fig. 1 XRD patterns of as-cast $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ and $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ alloys

Figure 2 shows the backscattered SEM micrograph of as-cast $\text{LaFe}_{10.9}\text{Co}_{0.7}\text{Si}_{1.4}$ alloy. The mixed matrix consists of the main black (position I) and white (position II) microstructures. According to the result of the EDS analysis of as-cast $\text{LaFe}_{10.9}\text{Co}_{0.7}\text{Si}_{1.4}$, shown in Table 1, the black and white microstructures are α -Fe and LaFeSi phases, respectively. There is a certain of grey microstructure around the black grain, and grey microstructure changes gradually from light grey to dark grey with the increase of Fe and the decrease of La and Si, which is corresponding to the diffusion process between α -Fe atom and La and Si atoms of LaFeSi phase. In the grey microstructure, there is a small amount of 1:13 phase around the α -Fe grain, which accords with the character of peritectic reaction: $\text{Fe} + \text{LaFeSi} \rightarrow \text{La}(\text{Fe}, \text{Si})_{13}$ [20]. In addition, Co can substitute Fe to form substitution solid solution in each phase of as-cast $\text{LaFe}_{10.9}\text{Co}_{0.7}\text{Si}_{1.4}$ alloy. Because of the random distribution of Si atoms on both Fe sites in LaCo_{13} -type $\text{LaFe}_{13-x}\text{Si}_x$ alloys, Si can be regarded as the substitution element for Fe in LaCo_{13} -type $\text{LaFe}_{13-x}\text{Si}_x$ alloys like the substitution of Co for Fe.

For further studying the effect of Co on the 1:13 phase formation in $\text{LaFe}_{13-x}\text{Si}_x$ alloys, Co is introduced

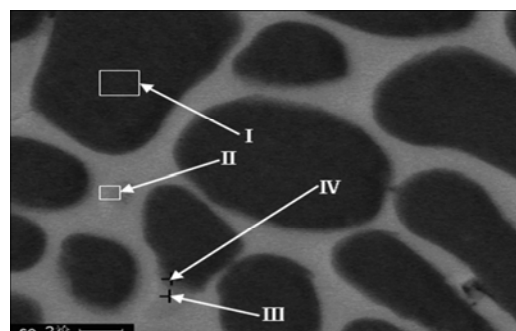


Fig. 2 Backscattered SEM image of as-cast $\text{LaFe}_{10.9}\text{Co}_{0.7}\text{Si}_{1.4}$

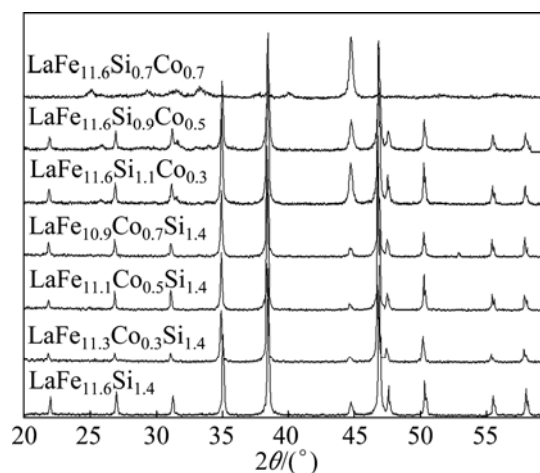
Table 1 EDS analysis of different positions in Fig. 1

Position	$x(\text{La})/\%$	$x(\text{Fe})/\%$	$x(\text{Co})/\%$	$x(\text{Si})/\%$	Phase
I	01.18	86.20	05.26	07.36	α -Fe
II	30.59	26.24	08.02	35.14	LaFeSi
III	27.21	37.17	07.64	27.99	Unknown
IV	11.99	69.69	05.80	12.53	1:13 phase

as the substitution element for Si in $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ alloys. The XRD patterns of as-cast $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ alloys show that the amounts of 1:13 and LaFeSi phases gradually decrease and the amount of α -Fe(Co,Si) solid solution increases with the increase of Co content, as shown in Fig. 1. When x reaches 0.7, there is almost only α -Fe(Co,Si) solid solution. This indicates that Co will hamper the formation of 1:13 and LaFeSi phases and improve the formation of α -Fe(Co, Si) solid solution in as-cast $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ alloys.

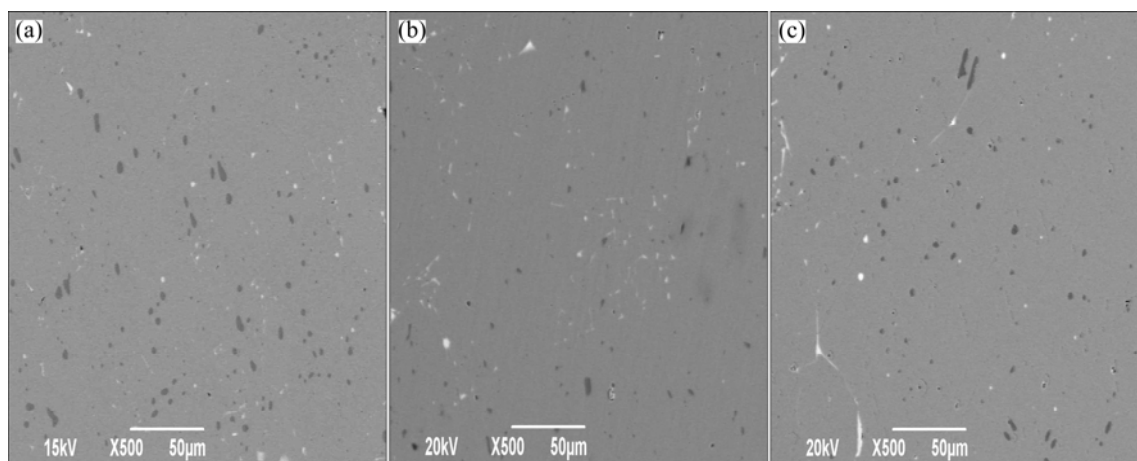
Figure 3 shows the XRD patterns of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ and $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ alloys annealed at 1523 K for 5 h. One can find that the annealed $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ alloys consist of the cubic 1:13 phase and a small amount of impurity phase of α -Fe. From the backscattered SEM micrographs of the annealed $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ alloys, as shown in Fig. 4, the amount of impurities including α -Fe and LaFeSi phases has no obvious change with the increase of Co content, which indicates that the introduction of Co as the substitution for Fe in $\text{LaFe}_{13-x}\text{Si}_x$ alloys cannot reduce the amount of impurities with the same annealing time or increase the diffuse reaction speed of $\text{Fe} + \text{LaFeSi} \rightarrow \text{La}(\text{Fe,Si})_{13}$. In the annealed $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ alloys, there is a certain amount of 1:13 phase when $x \leq 0.5$, but α -Fe is also a main phase. The annealed $\text{LaFe}_{11.6}\text{Si}_{0.7}\text{Co}_{0.7}$ alloy mainly consists of α -Fe(Co,Si) solid solution, while the amount of 1:13 phase is quite small.

Because the single LaCo_{13} -type structure can be obtained when the $\text{CeFe}_{13-x}\text{Si}_x$ ($2.4 \leq x \leq 2.6$) alloys are

**Fig. 3** XRD patterns of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ and $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ alloys annealed at 1523 K for 5 h

annealed for only 12 h [10], the substitution of Ce for La in $\text{LaFe}_{13-x}\text{Si}_x$ alloys may improve the formation or reduce the annealing time [21]. Figure 5 shows the XRD patterns of the as-cast $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{1.5}\text{Si}_{1.5}$ alloys ($0 \leq x \leq 0.5$), from which one can find that the main phases are α -Fe and LaFeSi phases, and the minor phase of 1:13 phase is observed in those alloys. When $x=0.33$, the amount of 1:13 phase is the largest, the diffraction peaks ratio of 1:13 phase is almost the same as that in other as-cast $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{1.5}\text{Si}_{1.5}$ alloys. In addition, there is a certain amount of $\text{Ce}_2\text{Fe}_{17}$ phase when x reaches 0.5, which indicates that the substitution of Ce for La in as-cast $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{1.5}\text{Si}_{1.5}$ alloys has some limits.

Our previous work showed that the $\text{Ce}_2\text{Fe}_{17}$ phase cannot be eliminated by annealing at 1373 K for 2 h + 1523 K for 5 h and then furnace cooling to room temperature [22]. In this work, the as-cast $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ alloys were annealed at 1523 K for 5 h and then furnace cooled to room temperature. Figure 6 shows XRD patterns of the annealed $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{1.5}\text{Si}_{1.5}$

**Fig. 4** Backscattered SEM micrographs of $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ annealed at 1523 K for 5 h: (a) $x=0$; (b) $x=0.5$; (c) $x=0.7$

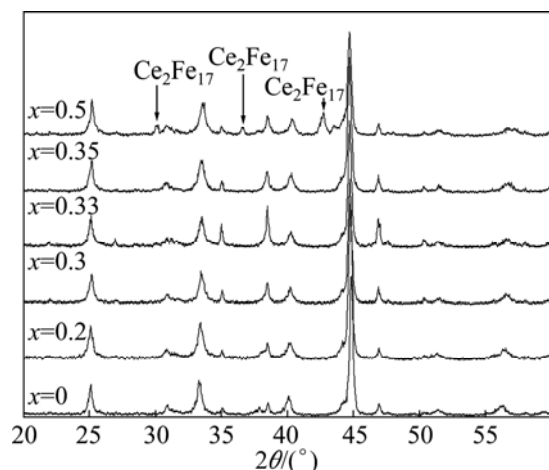


Fig. 5 XRD patterns of as-cast $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ alloys

alloys with $x=0, 0.1, 0.2, 0.33, 0.35$, and 0.5 , respectively. The main phase is 1:13 phase, and impurity phase is a small amount of $\alpha\text{-Fe}$ in $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ alloys for $0 \leq x \leq 0.33$. $\text{Ce}_2\text{Fe}_{17}$ phase begins to appear in $\text{La}_{0.65}\text{Ce}_{0.35}\text{Fe}_{11.5}\text{Si}_{1.5}$ alloy. There is a large amount of $\text{Ce}_2\text{Fe}_{17}$ phase when x reaches 0.5 . All of those indicate that the substitution of Ce for La in annealed $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ alloys also has some limits. The maximal Ce substitution for La to form continuous solid solution in annealed $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ alloys is $x=0.33\text{--}0.35$. In addition, the diffraction peaks of the cubic 1:13 phase have obvious shift to high angle with the increase of Ce content, as shown in Fig. 6. This is a signature of lattice contraction, which attributes to the radius of Ce (0.27 nm) which is smaller than that of La (0.278 nm). This also shows that Ce can substitute La in $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ alloys with LaCo_{13} -structure to form solid solution.

The backscattered SEM micrographs of $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ annealed at 1523 K for 5 h are shown

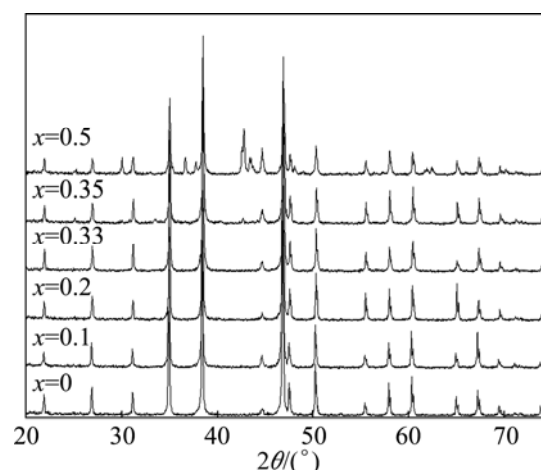


Fig. 6 XRD patterns of $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ alloys annealed at 1523 K for 5 h

in Fig. 7. One can find that there is small amount of $\text{Ce}_2\text{Fe}_{17}$ in $\text{La}_{0.67}\text{Ce}_{0.33}\text{Fe}_{11.5}\text{Si}_{1.5}$, which cannot almost be observed in the $\text{La}_{0.7}\text{Ce}_{0.3}\text{Fe}_{11.5}\text{Si}_{1.5}$. When x reaches 0.5 , and the $\text{Ce}_2\text{Fe}_{17}$ occupies about 30% in volume proportion. Those also show that the maximal Ce substitution for La to form continuous solid solution in $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ alloys is $x=0.33\text{--}0.35$. In addition, the EDS result of the annealed $\text{La}_{0.5}\text{Ce}_{0.5}\text{Fe}_{11.5}\text{Si}_{1.5}$ shows that the ratios of La and Ce in $\alpha\text{-Fe}(\text{Si})$ solid solution are 1.2% and 0.7% , respectively, which indicates that the solid solution range of La and Ce in $\alpha\text{-Fe}(\text{Si})$ solid solution is very small. In $\text{Ce}_2\text{Fe}_{17}$ alloy, there is certain amount of La and Si, thus $\text{Ce}_2\text{Fe}_{17}$ alloy should be the $(\text{La}, \text{Ce})_2(\text{Fe}, \text{Si})_{17}$ solid solution.

As grain refining agents in steel, B atoms are also introduced in the form of interstitial atoms in $\text{LaFe}_{13-x}\text{Si}_x\text{B}_y$ alloys. According to the XRD patterns of as-cast $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$ alloys, as shown in Fig. 8, the addition of B improves formation of the LaCo_{13} -type

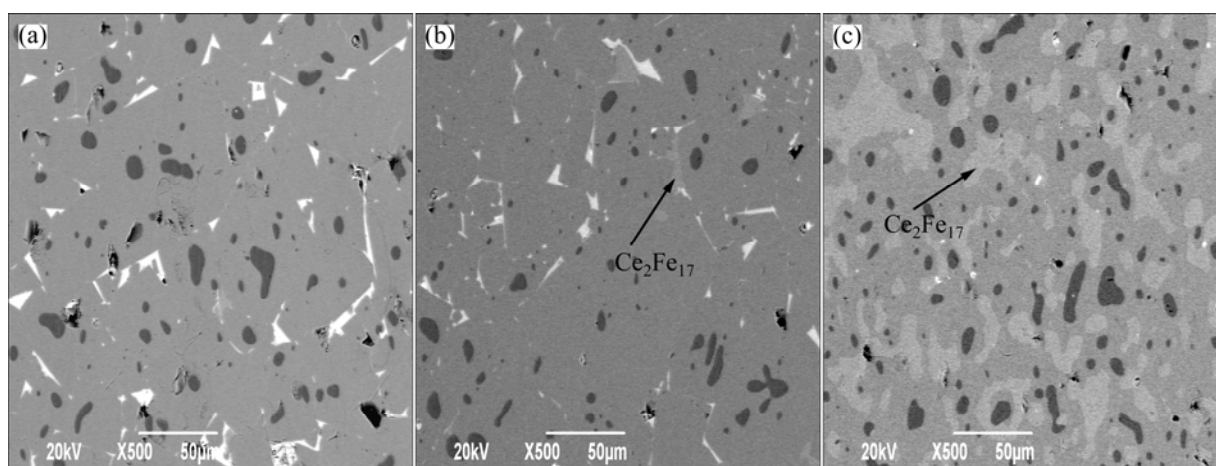


Fig. 7 Backscattered SEM micrographs of $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ annealed at 1523 K for 5 h : (a) $x=0.3$; (b) $x=0.33$; (c) $x=0.5$

phase in as-cast $\text{LaFe}_{13-x}\text{Si}_x$ alloys, and the amount of 1:13 phase increases with the increase of B content. But the introduction of B will result in the formation of Fe_2B phase and the amount also increases with the increase of B content. The effects of B as the substitution element for Fe or Si in $\text{LaFe}_{11.5}\text{B}_{0.4}\text{Si}_{1.1}$ and $\text{LaFe}_{11.6}\text{B}_{0.5}\text{Si}_{1.5}$ alloys on the magnetocaloric properties were studied in detail in Ref. [19], but the influence on the formation of 1:13 phase and microstructure has few reports. In Fig. 8, the XRD patterns of as-cast $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ alloys show that B as the substitution element for Fe can improve the formation of 1:13 phase. The amount of 1:13 phase increases with the increase of B content, and there is a large amount of 1:13 phase when x reaches 0.5. However, there is also Fe_2B phase, and the amount increases with the increase of B content like as-cast $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$ alloys. For the substitution of B for Si, the amount of 1:13 phase in as-cast $\text{LaFe}_{11.6}\text{Si}_{1.3}\text{B}_{0.1}$ or $\text{LaFe}_{11.6}\text{Si}_{1.1}\text{B}_{0.3}$ alloys is larger than that in $\text{LaFe}_{11.6}\text{Si}_{1.4}$, but is less than that in $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ or $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$ with the same B content. In the as-cast $\text{LaFe}_{11.6}\text{Si}_{0.7}\text{Co}_{0.7}$ alloy, there is almost only α -Fe solid solution [23].

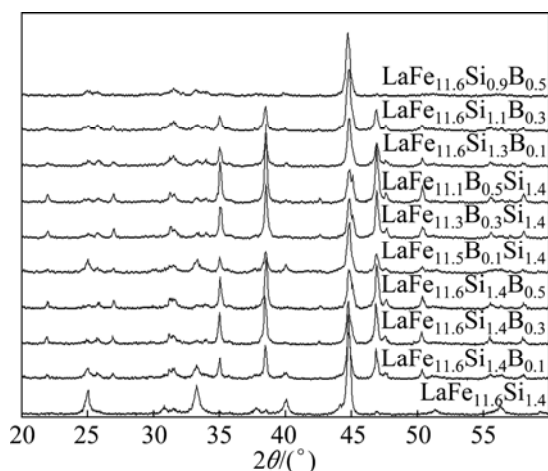


Fig. 8 XRD patterns of as-cast $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$, $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ and $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$ alloys

Our previous work showed that the Fe_2B phase cannot be eliminated by annealing at (1373 K, 1.5 h) + (1523 K, 5 h) and then furnace cooling to room temperature [23]. In this work, the as-cast $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$, $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ and $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$ alloys were annealed at 1523 K for 5 h and then furnace cooled to room temperature. In Fig. 9, the XRD patterns of the annealed $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$ and $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ alloys show that the main phase is 1:13 phase and the impurity includes α -Fe and Fe_2B phases, and the amount of Fe_2B phase increases with the increase of B content, which indicates that the annealing process in this work cannot eliminate Fe_2B phase. In the annealed $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$

alloys with $x=0.3$ and 0.5, there is a large amount of 1:13 phase besides α -Fe, which is different from the annealed $\text{LaFe}_{11.6}\text{Si}_{0.7}\text{Co}_{0.7}$ alloy. In addition, there is a certain amount of Fe_2B phase. In all, the introduction of B as interstitial atoms or the substitution for Fe in as-cast $\text{LaFe}_{13-x}\text{Si}_x$ alloys can obviously improve the formation of 1:13 phase, but the Fe_2B as accompanying phase of B introduction cannot be eliminated by high-temperature and short-time annealing. Thus there is a certain amount of Fe_2B phase in annealed $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$, $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ and $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$ alloys, and the amount increases with the increase of B content, which is harmful for the magnetocaloric effect [23]. Thus, how to hamper or eliminate Fe_2B phase needs further study.

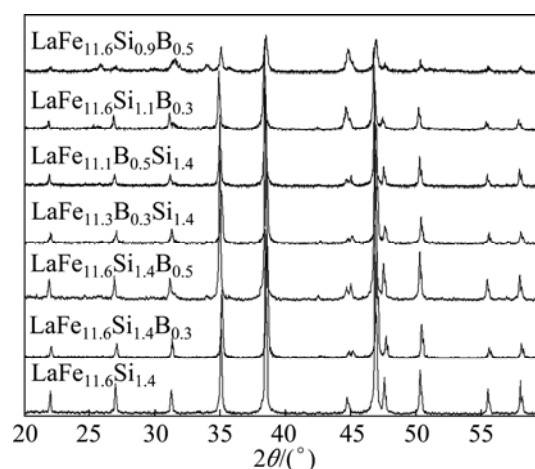


Fig. 9 XRD patterns of $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$, $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ and $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$ alloys annealed at 1523 K for 5 h

Figure 10 shows the backscattered SEM image of the annealed $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$ and $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ alloys with $x=0.1$ and 0.3, respectively. Compared with the microstructure of $\text{LaFe}_{11.6}\text{Si}_{1.4}$ annealed at 1523 K for 5 h, one can find that the grain of 1:13 phase is small and that of α -Fe is much larger. The Fe_2B and α -Fe mix, and locate the boundary of 1:13 phase grain. In addition, there is small white microstructure (LaFeSi phase) at the boundary of 1:13 phase grain.

On a whole, whether the substitution of Co for Si in $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ alloys or the substitution of B for Si in $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$ alloys both will make the formation of 1:13 phase difficult or the amount of 1:13 phase small compared with the same substituted amount of Co or B for Fe. Si element can be adjusted to the formation heat, and there is a critical value of Si content in $\text{LaFe}_{13-x}\text{Si}_x$ alloys. The formation heat is positive when the amount of Si is smaller than the critical value, which results in no 1:13 phase and only α -Fe solid solution when Co and B reach a certain amount in as-cast or annealed $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ and $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$ alloys. Thus, how to decrease the formation heat in substitution of Si deserves further study.

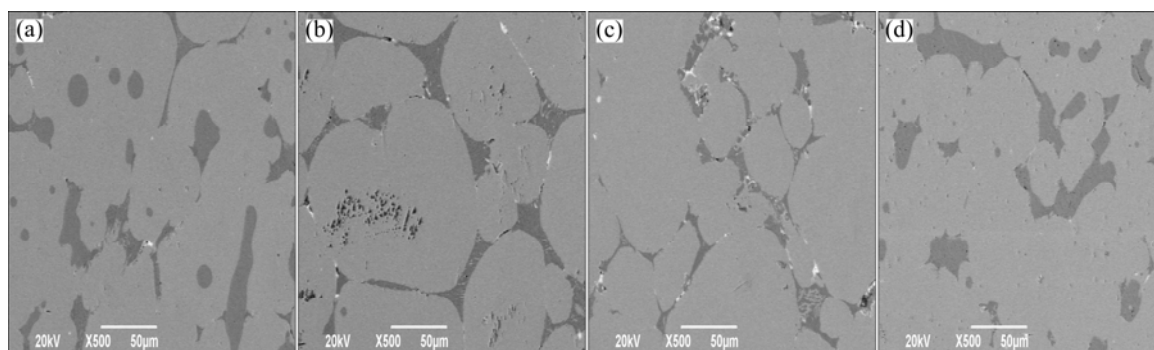


Fig. 10 Backscattered SEM images of $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$ and $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ alloys annealed at 1523 K for 5 h: (a) $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_{0.1}$; (b) $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_{0.3}$; (c) $\text{LaFe}_{11.5}\text{B}_{0.1}\text{Si}_{1.4}$; (d) $\text{LaFe}_{11.3}\text{B}_{0.3}\text{Si}_{1.4}$

4 Conclusions

Co can substitute Fe in different phases of as-cast $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ alloys and the amount of 1:13 phase increases when x reaches 0.7. But the introduction of Co cannot reduce the annealing time or increase the diffuse reaction speed, which results in the fact that the amounts of impurities including α -Fe and LaFeSi phases have no obvious change with the increase of Co content in annealed $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ alloys. B can improve the formation of 1:13 phase accompanied with Fe_2B phase in as-cast $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ and $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$ alloys. But the Fe_2B phase is kept and the amount increases with the increase of B in corresponding annealed alloys. Due to the increase of formation heat, the substitution of Co for Si in $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ alloys and the substitution of B for Si in $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$ alloys both will make the formation of 1:13 phase difficult or the amount of 1:13 phase small, and even no 1:13 phase and only α -Fe solid solution when Co and B reach a certain amount in as-cast and annealed $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ and $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$ alloys. The substitution of Ce for La has some limits in as-cast and annealed $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ alloys. $\text{Ce}_2\text{Fe}_{17}$ phase begins to be observed when x reaches 0.35, and the amount increases with the increase of Ce in annealed $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ alloys.

References

- [1] FUJITA A, FUKARAICHI K. Giant volume magnetostriction due to the itinerant electron metamagnetic transition in $\text{La}(\text{Fe},\text{Si})_{13}$ compounds [J]. *Magnetics, IEEE Transactions*, 1999, 35(5): 3796–3798.
- [2] HU F X, SHEN B G, SUN J R. Influence of negative lattice expansion and metamagnetic transition on magnetic entropy change in the compound $\text{LaFe}_{11.4}\text{Si}_{1.6}$ [J]. *Applied Physics Letters*, 2001, 78(23): 3675–3677.
- [3] FUKAMICHI K, FUJITA A, FUJIEDA S. Large magnetocaloric effects and thermal transport properties of $\text{La}(\text{Fe}, \text{Si})_{13}$ and their hydrides [J]. *Journal of Alloys and Compounds*, 2006, 408(412): 307–312.
- [4] FUJITA A, FUJIEDA S, FUKAMICHI K. Changes in electronic states and magnetic free energy in $\text{La}_{1-x}\text{Ce}_x(\text{Fe}_x\text{Si}_{1-x})_{13}$ magnetic refrigerants [J]. *Journal of Physics D: Applied Physics*, 2011, 44(6): 064013–064017.
- [5] WANG Fang-wei, WANG Guang-jun, HU Feng-xia, KURBAKOV A, SHEN Bao-gen, CHENG Zhao-hua. Strong interplay between structure and magnetism in the giant magnetocaloric intermetallic compound $\text{LaFe}_{11.4}\text{Si}_{1.6}$: A neutron diffraction study [J]. *Journal of Physics: Condensed Matter*, 2003, 15(30): 5269–5283.
- [6] FUJIEDA S, FUJITA A, FUKAMICHI K. Control of large magnetocaloric effects and hysteresis of $\text{La}_{1-x}\text{Ce}_x(\text{Fe}_{0.86}\text{Si}_{0.14})_{13}$ compounds [J]. *Magnetics, IEEE Transactions*, 2005, 41(10): 2787–2789.
- [7] XU Chao, LI Guo-dong, LI Xiao-wei, WANG Li-gang. Itinerant-electron metamagnetic transition and giant magnetic entropy change in $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}$ compound [J]. *Chinese Science Bulletin*, 2006, 51(17): 2046–2049.
- [8] FUJITA A, FUJIEDA S, FUKAMICHI K. Relative cooling power of $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ after controlling the Curie temperature by hydrogenation and partial substitution of Ce [J]. *Journal of Magnetism and Magnetic Materials*, 2007, 310(2): e1006–e1007.
- [9] WANG G F, SONG L, LI F A, OU Z Q, TEGUS O, BRUCK E, BUSCHOW K H J. Magnetocaloric effect in the $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4-x}\text{Co}_x\text{Si}_{1.6}$ compounds [J]. *Journal of Magnetism and Magnetic Materials*, 2009, 321(21): 3548–3552.
- [10] ZHAO Yan-ming, LIANG Jing-kui, TANG Wei-hua, GUO Yong-quan, RAO Guang-hui. Structure and magnetic properties of $\text{CeFe}_{13-x}\text{Si}_x$ compounds [J]. *Journal of Applied Physics*, 1995, 78(4): 2866–2867.
- [11] HU Feng-xia, SHEN Bao-gen, SUN Ji-rong, WANG Guan-jun, CHENG Zhao-hua. Very large magnetic entropy change near room temperature in $\text{LaFe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1}$ [J]. *Applied Physics Letters*, 2002, 80(5): 826–828.
- [12] SHEN Jun, LI Yang-xian, GAO Bo, SUN Ji-rong, SHEN Bao-gen. Magnetic properties and magnetic entropy changes of $\text{LaFe}_{11.0}\text{Co}_{0.8}(\text{Si}_{1-x}\text{Al}_x)_{1.2}$ compounds [J]. *Journal of Magnetism and Magnetic Materials*, 2007, 310(2): 2823–2825.
- [13] LIU Xu-bo, ALTOUNIAN Z. Effect of Co content on magnetic entropy change and structure of $\text{La}(\text{Fe}_{1-x}\text{Co}_x)_{11.4}\text{Si}_{1.6}$ [J]. *Journal of Magnetism and Magnetic Materials*, 2003, 264(2–3): 209–213.
- [14] ZHANG Hu, BAO Bo, SHI Pu-ji, FU Bin, LONG Yi, CHANG Yong-qin, WAN Fa-rong. Phase formation with NaZn_{13} structure in metamagnetic $\text{La}(\text{Fe}_{1-x}\text{Co}_x)_{11.9}\text{Si}_{1.1}$ compounds [J]. *Journal of Rare Earths*, 2008, 26(5): 727–730.

- [15] HUANG M Q, WALLACE W E, MCHENRY M E. Soft magnetic properties of LaCo_{13} and $\text{La}(\text{Co}, \text{Fe})_{13}$ alloys [J]. Journal of Applied Physics, 1998, 83(11): 6471–6473.
- [16] WANG F W, KURBAKOV A, WANG G J, HU F X, SHEN B G, CHENG Z H. Strong interplay between structure and magnetism in $\text{LaFe}_{11.3}\text{Co}_{0.6}\text{Si}_{1.1}$: A neutron diffraction study [J]. Physica B: Condensed Matter, 2006, 385–386: 343–345.
- [17] GAO B, HU F X, WANG J, SHEN J, SUN J R, SHEN B G. Influence of the substitution of Cu for Si on magnetic entropy change and hysteresis loss in $\text{LaFe}_{11.7}(\text{Si}_{1-x}\text{Cu}_x)_{1.3}$ compounds [J]. Journal of Applied Physics, 2009, 105(7): 07A916–07A918.
- [18] ZHANG H, LONG Y, CAO Q, MUDRYK Y A, ZOU M, GSCHNEIDNER JR K A, PECHARSKY V K. Microstructure and magnetocaloric effect in cast $\text{LaFe}_{11.5}\text{Si}_{1.5}\text{B}_x$ ($x=0.5, 1.0$) [J]. Journal of Magnetism and Magnetic Materials, 2010, 322(13): 1710–1714.
- [19] SHEN Jun, WANG Fang, ZHAO Jin-liang, WU Jian-feng, GONG Mao-qiong, HU Feng-xia, LI Yang-xian, SUN Ji-rong, SHEN Bao-gen. Reduction in hysteresis losses and large magnetic entropy change in the B-doped $\text{La}(\text{Fe}, \text{Si})_{13}$ compounds [J]. Journal of Applied Physics, 2010, 107: 09A909.
- [20] RAGHAVAN V. Fe–La–Si (Iron–lanthanum–silicon) [J]. Journal of Phase Equilibria, 2001, 22(2): 158–159.
- [21] XU Chao, LI Guo-dong, WANG Li-gang. Itinerant-electron metamagnetic transition and giant magnetocaloric effect in $\text{La}_{0.8}\text{Ce}_{0.2}\text{Fe}_{11.4}\text{Si}_{1.6}$ compound [J]. Journal of Applied Physics, 2006, 99: 123913–123916.
- [22] CHEN Xiang, CHEN Yun-gui, TANG Yong-bo. The effect of high-temperature annealing on $\text{LaFe}_{11.5}\text{Si}_{1.5}$ and the magnetocaloric properties of $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ compounds [J]. Rare Metals, 2011, 30(4): 343–347.
- [23] CHEN Xiang, CHEN Yun-gui, TANG Yong-bai. Phase, structural, and magnetocaloric properties of high temperature annealed $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{B}_x$ [J]. Journal of Alloys and Compounds, 2011, 509(6): 2864–2869.

Ce, Co, B 对 $\text{La}(\text{Fe}, \text{Si})_{13}$ 合金中 LaCo_{13} 结构 1:13 相形成的影响

陈 湘^{1,2}, 陈云贵¹, 唐永柏¹, 肖定全¹

1. 四川大学 材料科学与工程学院, 成都 610065;

2. 内江师范学院 工程技术学院, 内江 641002

摘 要: 通过 XRD、SEM、EDS 等方法, 研究 Ce、Co、B 对 $\text{La}(\text{Fe}, \text{Si})_{13}$ 合金中 LaCo_{13} 结构 1:13 相形成的影响。结果表明, 在铸态 $\text{LaFe}_{11.6-x}\text{Co}_x\text{Si}_{1.4}$ 合金中, Co 能够促进铸态 1:13 相的形成。但是在铸态以及热处理后的 $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ 合金中, Co 阻止 1:13 相的形成, 同时促进 $\alpha\text{-Fe}(\text{Co}, \text{Si})$ 固溶体相的形成。在铸态 $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ 合金中, 当 Ce 的含量达到一定值后, 合金中将有 $\text{Ce}_2\text{Fe}_{17}$ 相形成, 且随着 Ce 含量的增加而增加。在铸态 $\text{LaFe}_{11.6-x}\text{B}_x\text{Si}_{1.4}$ 合金中, B 能够促进 1:13 相的形成, 但同时会有 Fe_2B 相产生。在铸态以及热处理后的 $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{Co}_x$ 和 $\text{LaFe}_{11.6}\text{Si}_{1.4-x}\text{B}_x$ 合金中, Co 能够促进 $\alpha\text{-Fe}(\text{Co}, \text{Si})$ 固溶体相的形成。在 $\text{LaFe}_{11.6}\text{Si}_{0.9}\text{B}_{0.5}$ 合金中, 基本上只有 $\alpha\text{-Fe}(\text{Co}, \text{Si})$ 固溶体相存在, 这点与 $\text{LaFe}_{11.6}\text{Si}_{0.7}\text{Co}_{0.7}$ 合金相似。在高温短时热处理制备的 $\text{La}(\text{Fe}, \text{Si})_{13}$ 合金中, 引入 Ce、Co、B 并不能消除杂相 $\alpha\text{-Fe}$, 且同时会伴随新的杂相产生, 如 $\text{Ce}_2\text{Fe}_{17}$ 和 Fe_2B 相。

关键词: $\text{LaFe}_{13-x}\text{Si}_x$ 合金; 高温短时热处理; 1:13 相

(Edited by Hua YANG)