Solidification microstructure and phase transition of La-Nd-Fe alloys

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Abstract
The solidification microstructure and phase transition of ten La-Nd-Fe alloys were studied experimentally by scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS) and differential thermal analysis (DTA). Phase compositions and phase transition temperatures of La-Nd-Fe alloys were measured and the formed phases were identified. The solidification behavior of La-Nd-Fe alloys was analyzed based on the experimental results of both solidification microstructure and phase transitions with the reported Nd-Fe, La-Fe and La-Nd sub-binary phase diagrams. The results indicated that the solidification processes of all La-Nd-Fe alloys begin with the precipitation of primary phase fcc(γ-Fe) and then follow by the formation of bcc(α-Fe) and/or Fe17Nd2 phases through different peritectic reactions. The solidification microstructure of three Fe65La29Nd6, Fe65La25Nd10 and Fe65La23Nd13 alloys presents three-phase microstructure with bcc(α-Fe), Fe17Nd3 and fcc(La,Nd) phases, while that of three Fe65La39Nd14, Fe65La9Nd36 and Fe65La15.5Nd19.5 alloys shows three-phase microstructure with bcc(α-Fe), Fe17Nd2 and dhcp(La,Nd) phases. The two-phase microstructure with Fe17Nd2 and dhcp(La,Nd) phases was formed in the solidification microstructure of four Fe65La12Nd23, Fe65La6.5Nd28.5, Fe65La4Nd31 and Fe65La1.5Nd33.5 alloys. Moreover, no stable ternary intermetallic compound was found in the present experiments. The solidification microstructure and phase transition of La-Nd-Fe alloys would provide a basis for the design of La-Nd-Fe-B magnetic alloys.

1. Introduction
Nd-Fe-B permanent magnets have excellent magnetic performances and have been widely used in the wind-power, electric vehicles and other fields [1–8]. The superiority of these magnets arises from the large saturation magnetization and high anisotropy field of Nd2Fe14B main phase [9–12]. During the solidification process, the primary phase fcc(γ-Fe) (transformed to bcc(α-Fe) phase at low temperature) precipitates from Nd-Fe-B-based alloy melts at high temperature, and then Nd2Fe14B main phase is formed by the peritectic reaction, L + γ-Fe → Nd2Fe14B [13, 14]. As the results, Nd-Fe-B-based alloys contain normally Nd2Fe14B main phase and α-Fe minor phase. In order to improve greatly the volume fraction of Nd2Fe14B main phase in the magnets, it is crucial to reduce the amounts of the deteriorated α-Fe minor phase during the solidification process. Strip-Casting (SC) technology as one of rapid solidification technologies has been used widely in the production of Nd2Fe14B-based permanent magnets [14–19]. The high cooling rates in the solidification process would restrain the precipitation of the primary phase γ-Fe from under-cooled melts, which is the most effective method to control the formation of α-Fe phase in the Nd-Fe-B-based magnets. Therefore, the microstructure evolution of Nd-Fe-B-based alloys during the solidification process is significant effect on their magnetic properties [11, 18, 19].

On the other hand, Nd-Fe-B permanent magnets were needed to the low-abundant and expensive heavy rare-earth metals Dy and Tb to achieve higher coercivity and better thermal stability [20, 21]. It has limited the development of Nd-Fe-B magnets. In contrast, the high-abundant and cheap light rare-earth metals La, Ce and
Y are overstocked. To balance the use of rare-earth metals, the application of the high-abundant rare-earth metals La, Ce and Y in Nd-Fe-B magnets to replace the part of heavy rare-earth metals is an effective and promising way to develop novel Nd-Fe-B permanent magnets [22–28]. Recently, it has been reported that Nd-Fe-B magnets with La would exhibit a good magnetic performance [23, 25, 28]. For example, (Nd0.4La0.6)15Fe77.5B7.5 melt-spun ribbon prepared with the wheel speed of 26 m s$^{-1}$ shows better magnetic properties ($H_{ci}$ = 7.27 kOe, $M_r$ = 90.94 emu g$^{-1}$, $(BH)_{max}$ = 12.10 MGOe) [28]. In order to better understand the effect of La on phase formation, microstructure, phase transition and magnetic properties of Nd-Fe-B-based permanent magnet, the solidification behavior of La-Nd-Fe-B alloys is fundamental. Therefore, as a key ternary system in La-Nd-Fe-B alloys, the solidification microstructure and phase transition of La-Nd-Fe alloys were studied experimentally in this work.

| Table 1. Phase compositions and identified phases of La-Nd-Fe alloys. |
|-----------------------------|--------|--------|--------|-----------------------------|
| Nominal composition of alloys (at.%) | Condition | EDS measurement (at.%) | Phase identification |
| Fe$_{65}$La$_{29}$Nd$_6$ | as-cast | Fe 99.37 La 0.04 Nd 0.79 | fcc($\gamma$-Fe) |
| | annealed | Fe 88.23 La 0.31 Nd 0.41 | fcc(La,Nd) |
| Fe$_{65}$La$_{32}$Nd$_{10}$ | as-cast | Fe 99.20 La 0.43 Nd 0.37 | fcc($\gamma$-Fe) |
| | annealed | Fe 88.25 La 1.86 Nd 9.89 | Fe$_2$Nd$_2$ |
| Fe$_{65}$La$_{22}$Nd$_{13}$ | as-cast | Fe 99.14 La 0.40 Nd 0.46 | fcc($\gamma$-Fe) |
| | annealed | Fe 88.59 La 1.50 Nd 9.91 | Fe$_2$Nd$_2$ |
| Fe$_{65}$La$_{19}$Nd$_{16}$ | as-cast | Fe 98.07 La 1.32 Nd 0.61 | fcc($\gamma$-Fe) |
| | annealed | Fe 90.47 La 1.32 Nd 8.21 | Fe$_2$Nd$_2$ |
| Fe$_{65}$La$_{14}$Nd$_{26}$ | as-cast | Fe 89.28 La 0.12 Nd 0.60 | fcc($\gamma$-Fe) |
| | annealed | Fe 88.98 La 0.59 Nd 10.43 | Fe$_2$Nd$_2$ |
| Fe$_{65}$La$_{15.5}$Nd$_{19.5}$ | as-cast | Fe 98.75 La 0.31 Nd 0.94 | fcc($\gamma$-Fe) |
| | annealed | Fe 88.61 La 0.94 Nd 10.45 | Fe$_2$Nd$_2$ |
| Fe$_{65}$La$_{12}$Nd$_{23}$ | as-cast | Fe 89.17 La 0.47 Nd 10.36 | fcc($\gamma$-Fe) |
| | annealed | Fe 89.17 La 0.47 Nd 10.36 | Fe$_2$Nd$_2$ |
| Fe$_{65}$La$_{6.5}$Nd$_{28.5}$ | as-cast | Fe 89.11 La 0.40 Nd 10.49 | fcc($\gamma$-Fe) |
| | annealed | Fe 89.11 La 0.40 Nd 10.49 | Fe$_2$Nd$_2$ |
| Fe$_{65}$La$_{4}$Nd$_{31}$ | as-cast | Fe 88.64 La 0.34 Nd 11.02 | fcc($\gamma$-Fe) |
| | annealed | Fe 88.64 La 0.34 Nd 11.02 | Fe$_2$Nd$_2$ |
| Fe$_{65}$La$_{1.5}$Nd$_{33.5}$ | as-cast | Fe 88.91 La 0.03 Nd 11.06 | fcc($\gamma$-Fe) |
| | annealed | Fe 88.91 La 0.03 Nd 11.06 | Fe$_2$Nd$_2$ |

2. Experimental procedure

2.1. Sample preparation
La-Nd-Fe alloy samples were prepared from the pure metals of La (purity, 99.9%), Nd (purity, 99.9%) and Fe (purity, 99.9%). The alloys samples were melted four times by non-consumable tungsten electrode under an argon atmosphere protection to ensure homogeneity of the composition. The weight loss during the arc-melting was less than 1% and thus their compositions were considered to approach their nominal ones. In order to achieve composition homogeneity and prevent the samples oxidation, La-Nd-Fe alloy samples were sealed in evacuated quartz tubes under vacuum ($<10^{-3}$Pa) to be annealed at 873 K for 1440 h in a high-precision diffusion furnace, and then quickly quench into ice water to maintain microstructure at certain temperature.
### Table 2. Phase transition and solidification process of La-Nd-Fe alloys.

| Nominal composition of alloys (at.%) | Thermal signals | Phase transition | Solidification process |
|-------------------------------------|-----------------|------------------|------------------------|
| Fe<sub>65</sub>La<sub>9</sub>Nd<sub>26</sub> | 1298.1/1292.1   | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(α-Fe) + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |
| Fe<sub>65</sub>La<sub>12</sub>Nd<sub>13</sub> | 1329.5/1325.4   | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |
| Fe<sub>65</sub>La<sub>15</sub>Nd<sub>19.5</sub> | 1423.4/1377.1   | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |
| Fe<sub>65</sub>La<sub>18</sub>Nd<sub>16</sub> | 1027.9/1034.1   | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |
| Fe<sub>65</sub>La<sub>22</sub>Nd<sub>13</sub> | 1395.7/1390.7   | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |
| Fe<sub>65</sub>La<sub>25</sub>Nd<sub>10</sub> | 1210.9/1158.6   | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |
| Fe<sub>65</sub>La<sub>29</sub>Nd<sub>6</sub> | 1214.0/1162.3   | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |
| Fe<sub>65</sub>La<sub>6.5</sub>Nd<sub>28.5</sub> | 1446.2/1378.8   | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |
| Fe<sub>65</sub>La<sub>1.5</sub>Nd<sub>33.5</sub> | 1470.8/1379.8   | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |
| Fe<sub>65</sub>La<sub>4</sub>Nd<sub>31</sub> | 1467.0/1401.7   | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |
| Fe<sub>65</sub>La<sub>3</sub>Nd<sub>26.5</sub> | 985.2/995.5     | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |
| Fe<sub>65</sub>La<sub>6</sub>Nd<sub>18.5</sub> | 995.8/995.5     | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |
| Fe<sub>65</sub>La<sub>1</sub>Nd<sub>35.5</sub> | 995.8/995.5     | L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> | L → L + fcc(γ-Fe) → L + Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) |

**Thermal signals**
- **Heating/K**: 1214.0, 1047.2, 1210.9, 1061.1, 1252.8, 1041.4, 1298.1, 1027.9, 1423.4, 1329.5, 1021.4, 1370.7, 1004.7, 1446.2, 985.2, 1467.0, 995.8, 1470.8, 995.5
- **Cooling/K**: 1162.3, 1051.2, 1158.6, 1054.2, 1169.9, 1034.1, 1292.1, 1377.1, 996.3, 1325.4, 1023.1, 1307.6, 1035.5, 1378.8, 995.5, 1401.7, 971.1, —

**Phase transition**
- Fe<sub>17</sub>Nd<sub>2</sub> (bcc, α-Fe)
- Fe<sub>17</sub>Nd<sub>2</sub> (fcc, γ-Fe)
- Fe<sub>17</sub>Nd<sub>2</sub> (dhcp, La,Nd)

**Solidification process**
- L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd)
- L + fcc(γ-Fe) → Fe<sub>17</sub>Nd<sub>2</sub> + fcc(La,Nd) + fcc(La,Nd)
2.2. Microstructure characterization
For solidification microstructure examination, considering the easy oxidization of rare-earth metals, La-Nd-Fe alloy samples were prepared under the condition of ethyl alcohol absolute. The alloy samples were prepared with the standard metallographic procedure. The alloy samples were first ground using silicon carbide paper and then polished with diamond with approximately 0.05 μm particle sizes. The alloy samples were ultrasonically cleaned in ethyl alcohol absolute for 300 s after each step of grinding and polishing. The microstructure of the alloy samples was examined using scanning electron microscopy (SEM) using back scattered electron (BSE) mode and the phase compositions of alloy samples were measured using energy-dispersive x-ray spectra (EDS).

2.3. Thermal analysis
To determine the temperatures of phase transitions in La-Nd-Fe alloy samples, thermal analysis measurements were carried out using Al2O3 crucibles under a flow of pure N2 atmosphere. The instrument calibration was carried out using calibration metals In, Sn, Bi, Zn, Al, Ag, Au and Ni as standard samples to reduce the random and systematic errors. The high-purity Al2O3 crucibles were employed in the thermal analysis experiments. The alloy samples about 15–20 mg were measured by heating up to 1673 K and cooling down to 373 K at both heating and cooling rates of 20 K min⁻¹. The accuracy of the present measurements is evaluated to be within ±1 K in the measured temperature range.

3. Results and discussion
The microstructure characterization and thermal analysis measurements of La-Nd-Fe alloy samples were carried out in this work. The phase compositions of La-Nd-Fe alloy samples measured by EDS were summarized in table 1. Based on the thermal analysis curves of the alloy samples, the onset temperature of the peak was determined as the reactions, while the last peak temperature was selected to be the liquidus temperature. Table 2

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Figure 1. Back-scattered electron (BSE) micrograph of (a) as-cast and (b) annealed Fe₆₅La₂₉Nd₆ alloy.
shows phase transition temperatures and solidification sequences of La-Nd-Fe alloy samples according to thermal analysis results and the solidification microstructure analysis based on the reported Nd-Fe, La-Fe and La-Nd sub-binary phase diagrams [29–31].

3.1. Solidification microstructure

Figure 1 is the BSE micrograph of as-cast and annealed Fe65La29Nd6 alloy. As shown in figure 1(a), the gray dark phase is the primary phase fcc(γ-Fe) (Fe99.37-La0.04-Nd0.79), which would transform to bcc(α-Fe) phase at low temperature, while the white phase is fcc(La,Nd) (Fe1.71-La83.08-Nd15.21) phase according to the EDS results in table 1. The reported Fe-Nd binary phase diagram [29] shows that Fe17Nd2 phase is formed by the peritectic reaction, L + fcc(γ-Fe) → Fe17Nd2 at 1490.2 K, while the La-Nd binary phase diagram shows fcc(La,Nd) phase in the rich-La part and dhcp(La,Nd) phase in the rich-Nd part [30]. Figure 1(b) is the BSE micrograph of the alloy annealed at 873 K for 1440 h. The gray black phase with the composition of Fe99.32-La0.31-Nd0.37 is fcc(γ-Fe) phase, while the grey phase around fcc(γ-Fe) phase is Fe17Nd2 (Fe88.23-La2.36-Nd9.41) phase with the solubility of La. The bright phase is fcc(La,Nd) (Fe1.93-La82.75-Nd15.32) phase from the EDS results. The lamellar two-phase microstructure with fcc(La,Nd) and Fe17Nd2 phases was exhibited near the primary phase fcc(γ-Fe), which indicates Fe17Nd2 phase formed by the peritectic reaction, L + fcc(γ-Fe) → Fe17Nd2. The white gray phase along Fe17Nd2 phase is fcc(La,Nd) phase from the EDS results (Fe1.93-La82.75-Nd15.32). The lamellar two-phase microstructure with fcc(La,Nd) and Fe17Nd2 phases was
observed clearly, which was formed through the reaction, $L \rightarrow \text{fcc}(\text{La,Nd}) + \text{Fe}_{17}\text{Nd}_2$. The microstructure of as-cast $\text{Fe}_{65}\text{La}_{22}\text{Nd}_{13}$ alloy in figure 2(b) contains fcc($\gamma$-Fe), $\text{Fe}_{17}\text{Nd}_2$, fcc(La,Nd) three phases, and shows the two-phase microstructure with fcc(La,Nd) and $\text{Fe}_{17}\text{Nd}_2$ phases, which is similar to the microstructure of as-cast $\text{Fe}_{65}\text{La}_{25}\text{Nd}_{10}$ alloy.

Figure 3 displays the BSE micrograph of as-cast $\text{Fe}_{65}\text{La}_{19}\text{Nd}_{16}$ and $\text{Fe}_{65}\text{La}_{9}\text{Nd}_{26}$ alloys. In figure 3(a), the rare-earth phase in $\text{Fe}_{65}\text{La}_{19}\text{Nd}_{16}$ alloy is dhcp(La,Nd) phase rather than fcc(La,Nd) phase. It was explained that there is a phase transition from fcc(La,Nd) phase to dhcp(La,Nd) phase with the increase of Nd content according to the La-Nd binary phase diagram $[30]$. According to the EDS results in table 1, three different phases, e.g. bcc($\alpha$-Fe), $\text{Fe}_{17}\text{Nd}_2$ and dhcp(La,Nd), were identified in the BSE image as shown in figure 3(a). Figure 3(b) is the BSE micrograph of as-cast $\text{Fe}_{65}\text{La}_{19}\text{Nd}_{16}$ alloy. As can be seen, the solidification microstructure of as-cast $\text{Fe}_{65}\text{La}_{19}\text{Nd}_{16}$ alloy is similar with that of $\text{Fe}_{65}\text{La}_{19}\text{Nd}_{16}$ alloy, which consists of fcc($\gamma$-Fe), $\text{Fe}_{17}\text{Nd}_2$, dhcp(La,Nd) phases and the two-phase microstructure with $\text{Fe}_{17}\text{Nd}_2$ and dhcp(La,Nd) phases.

Figure 4 presents the BSE micrograph of as-cast and annealed $\text{Fe}_{65}\text{La}_{15.5}\text{Nd}_{19.5}$ alloy. Based on the EDS results in table 1, three phases, e.g. fcc($\gamma$-Fe), $\text{Fe}_{17}\text{Nd}_2$ and dhcp(La,Nd) phases were identified in the microstructure as shown in figure 4(a), and the two-phase microstructure with $\text{Fe}_{17}\text{Nd}_2$ and dhcp(La,Nd) phases is displayed. However, the microstructure of annealed alloy in figure 4(b) shows three different phases. The dark gray with lamellar structure is $\text{Fe}_{17}\text{Nd}_2$ phase, while the gray phase and light gray phase are Nd-rich dhcp(La,Nd) (Fe1.54-La13.08-Nd85.38) phase and La-rich dhcp(La,Nd) (Fe0.28-La60.86-Nd38.86) phase, respectively. Compared with the microstructure of as-cast alloy, fcc($\gamma$-Fe) phase disappears because fcc($\gamma$-Fe) phase transforms to form $\text{Fe}_{17}\text{Nd}_2$ phase through the peritectic reaction. Therefore, $\text{Fe}_{65}\text{La}_{15.5}\text{Nd}_{19.5}$ alloy undergoes the phase transition, $L \rightarrow \text{Fe}_{17}\text{Nd}_2 + $ dhcp(La,Nd) and three-phase field fcc($\gamma$-Fe) + $\text{Fe}_{17}\text{Nd}_2 + $ dhcp(La,Nd) during the solidification process. On the basis of the reported results $[6, 32]$, the La–Nd–Fe ternary system shows a three-phase eutectic transition and equilibrium three-phase region for the four-phase U-type reaction, $L + $ fcc($\gamma$-Fe) $\rightarrow \text{Fe}_{17}\text{Nd}_2 + $ dhcp(La,Nd).
Figure 5 shows the solidification microstructure of four as-cast Fe65La12Nd23, Fe65La6.5Nd28.5, Fe65La4Nd31 and Fe65La1.5Nd33.5 alloys. Compared with the solidification microstructure of as-cast Fe65La19Nd16 alloy, the microstructure of these four as-cast alloys indicates that the formation of dhcp (La, Nd) phase, although the phase transition from fcc (La, Nd) phase to dhcp (La, Nd) phase was not occurred according to the La-Nd binary phase diagram [30]. The microstructure of these four alloys displays similar solidification characteristics. On basis of the EDS results in table 1, these four alloys consist of angular strip structure and the continuous Fe17Nd2 phase. The two-phase microstructure with dhcp (La, Nd) and Fe17Nd2 phases was found, which indicated that the phase transition, L $\rightarrow$ dhcp (La, Nd) + Fe17Nd2, occurred during the solidification process.

3.2. Phase transition

Figure 6 is the thermal analysis curves of as-cast Fe65La22Nd10, Fe65La25Nd10 and Fe65La22Nd13 alloys. From the heating curve in figure 6(a), two exothermic peaks were observed clearly. Based on the microstructure analysis as shown in figure 1 and the Nd-Fe binary phase diagram [29], the high temperature peak at 1214.0 K is corresponding to the formation of Fe17Nd2 phase through the reaction, L + fcc ($\gamma$-Fe) $\rightarrow$ Fe17Nd2, while the low temperature peak at 1047.2 K is corresponding to the formation of fcc (La, Nd) phase through the reaction, L $\rightarrow$ Fe17Nd2 + fcc (La, Nd). As shown in the thermal analysis curves of Fe65La22Nd10 alloy in figure 6(b), the first peak at 1061.1 K is corresponding to the phase transition, L $\rightarrow$ fcc (La, Nd) + Fe17Nd2, while another peak at 1210.9 K is the transition temperature of formation of Fe17Nd2 phase during the solidification process in combination with the solidification microstructure analysis in figure 2(a). The solidification microstructure of Fe65La23Nd10 alloy is composed of fcc (La, Nd), Fe17Nd2 and bcc (α-Fe) (transformed from fcc ($\gamma$-Fe) phase) phases. As a result, the solidification process of Fe65La23Nd10 alloy can be described as: L $\rightarrow$ L + fcc ($\gamma$-Fe) $\rightarrow$ L + Fe17Nd2 $\rightarrow$ bcc (α-Fe) + fcc (La, Nd) + Fe17Nd2. In figure 6(c), the thermal analysis curves of Fe65La22Nd13 alloy shows that the two peaks (1252.8 K and at 1041.4 K) are consistent with the formation of Fe17Nd2 phase and two-phase fcc (La, Nd) + Fe17Nd2, based on the microstructure.
characterization in figure 2(b) and the Nd-Fe binary phase diagram. Therefore, the solidification path of Fe65La12Nd3 alloy is the same as that of Fe65La22Nd3 alloy.

Figure 7 presents the thermal analysis curves of as-cast Fe65La19Nd16, Fe65La9Nd26, and Fe65La4Nd31 alloys. As can be seen in figure 7(a), the thermal analysis curves of Fe65La19Nd16 alloy shows that the high temperature peak at 1298.1 K is corresponding to the reaction, $L \rightarrow Fe_{17}Nd_2$, while the low temperature peak at 1027.9 K belongs to the reaction, $L \rightarrow Fe_{17}Nd_2 + dhcp$(La,Nd) based on the similar analysis mentioned above. However, the transition temperature of $fcc$(La,Nd) phase to dhcp(La,Nd) phase was not measured in this work due to small thermal effect of solid phase transformation. It was noted that the high-temperature phase $fcc$(γ-Fe) transforms into $bcc$(α-Fe) phase at low temperature. It means that the thermal analysis results are in good consistent with the solidification microstructure in figure 3(a). It was concluded that the solidification behavior of Fe65La19Nd16 alloy can be expressed as $L \rightarrow L + fcc$(γ-Fe) $\rightarrow L + Fe_{17}Nd_2 \rightarrow L + fcc$(La,Nd) $\rightarrow bcc$(α-Fe) + dhcp(La,Nd) + $Fe_{17}Nd_2$.

Based on the thermal analysis curves in figure 7(b), the solidification behavior of Fe65La9Nd36 alloy is similar with that of Fe65La19Nd16 alloy. The peritectic reaction, $L + fcc$(γ-Fe) $\rightarrow Fe_{17}Nd_2$ occurs at 1423.4 K, while the formation of $Fe_{17}Nd_2 + dhcp$(La,Nd) phase occurs at 1000.7 K. In figure 7(c), the thermal analysis curves of Fe65La15.3Nd19.5 alloy show that the first peak at 1021.4 K is corresponding to the reaction, $L \rightarrow Fe_{17}Nd_2 + dhcp$(La,Nd), while the another peak at 1329.5 K is the temperature of the reaction, $L + fcc$(γ-Fe) $\rightarrow Fe_{17}Nd_2$. The results are consistent with the solidification microstructure as given in figure 4. Similar to the results of Fe65La15.3Nd16 alloy, $fcc$(γ-Fe) phase transforms to $bcc$(α-Fe) phase in final solidification microstructure. Therefore, the solidification process of Fe65La15.3Nd19.5 alloy can be shown as $L \rightarrow L + fcc$(γ-Fe) $\rightarrow L + Fe_{17}Nd_2 \rightarrow L + fcc$(La,Nd) $\rightarrow Fe_{17}Nd_2$ $\rightarrow bcc$(α-Fe) + dhcp(La,Nd) + $Fe_{17}Nd_2$.

The phase transition temperatures of Fe65La12Nd3, Fe65La15.3Nd19.5, Fe65La9Nd31 and Fe65La15.3Nd33.5 alloys were determined from the thermal analysis curves as shown in figure 8. The peritectic reaction, $L + fcc$(γ-Fe) $\rightarrow Fe_{17}Nd_2$, occurred at high temperature. Compared with the experimental results of six alloys discussed above, $fcc$(γ-Fe) phase was not observed in the solidification microstructure, while the proportion of Fe17Nd2 phase increases due to the transformation of $fcc$(γ-Fe) phase to form $Fe_{17}Nd_2$ phase during the solidification process. The solidification behavior of these four alloys can be expressed as $L \rightarrow L + fcc$(γ-Fe) $\rightarrow L + Fe_{17}Nd_2 \rightarrow Fe_{17}Nd_2 + dhcp$(La,Nd).
4. Conclusions

In this work, the solidification process of La-Nd-Fe alloys was analyzed based on the experimental investigation of solidification microstructure and phase transitions with the reported Nd-Fe, La-Fe and La-Nd sub-binary phase diagrams. The results shows that the solidification processes of three Fe$_{65}$La$_{29}$Nd$_{6}$, Fe$_{65}$La$_{25}$Nd$_{10}$ and Fe$_{65}$La$_{22}$Nd$_{13}$ alloys were described as L $\rightarrow$ L + fcc($\gamma$-Fe) $\rightarrow$ L + Fe$_{17}$Nd$_{2}$ $\rightarrow$ bcc($\alpha$-Fe) + Fe$_{17}$Nd$_{2}$ + fcc(La,Nd), whereas

Figure 6. Thermal analysis curves of as-cast (a) Fe$_{65}$La$_{29}$Nd$_{6}$, (b) Fe$_{65}$La$_{25}$Nd$_{10}$ and (c) Fe$_{65}$La$_{22}$Nd$_{13}$ alloys.
The solidification behaviors of three Fe$_{65}$La$_{19}$Nd$_{16}$, Fe$_{65}$La$_{15.5}$Nd$_{19.5}$ and Fe$_{65}$La$_{9}$Nd$_{26}$ alloys were expressed as $L \rightarrow L + fcc(\gamma$-$Fe) \rightarrow L + Fe_{17}Nd_2 \rightarrow L + Fe_{17}Nd_2 + fcc(La,Nd) \rightarrow bcc(\alpha$-$Fe) + Fe_{17}Nd_2 + dhcp(La,Nd). The solidification sequences of four Fe$_{65}$La$_{12}$Nd$_{23}$, Fe$_{65}$La$_{6.5}$Nd$_{28.5}$, Fe$_{65}$La$_{3}$Nd$_{33.5}$ and Fe$_{65}$La$_{1.5}$Nd$_{33.5}$ alloys were followed as $L \rightarrow L + fcc(\gamma$-$Fe) \rightarrow L + Fe_{17}Nd_2 \rightarrow Fe_{17}Nd_2 + dhcp(La,Nd). Additionally, no stable ternary compound was found in the present experiments. The experimental results of both solidification microstructure and phase transition in La-Nd-Fe alloys would be useful for the design of La-Nd-Fe-B magnetic alloys.

Figure 7. Thermal analysis curves of as-cast (a) Fe$_{65}$La$_{19}$Nd$_{16}$, (b) Fe$_{65}$La$_{15.5}$Nd$_{19.5}$ and (c) Fe$_{65}$La$_{13.5}$Nd$_{19.5}$ alloys.
Figure 8. Thermal analysis curves of as-cast alloys with different compositions. (a) Fe₆₅La₁₂Nd₂₃ alloy, (b) Fe₆₅La₆.₅Nd₂₈.₅ alloy, (c) Fe₆₅La₄Nd₃₁ alloy, (d) Fe₆₅La₁.₅Nd₃₃.₅ alloy.
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