Synchronous improvement in thermal conductivity and mechanical properties of Al–7Si–0.6Fe–0.5Zn cast alloy by B/La/Sr composite modification

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Abstract
In this paper, the effects of four modification processes (B, Sr, B/Sr and B/La/Sr modification process) on the thermal conductivity and mechanical properties of base alloy (Al–7Si–0.6Fe–0.5Zn) were systematically studied. Compared with the base alloy, different modification processes could synchronously improve the thermal conductivity and integrated mechanical properties by different degree. The synchronous improvement of B/0.15La/Sr composite modified alloy was the highest among all modified alloys, and the increasing rate of thermal conductivity, elongation and UTS were 25.6%, 150.2% and 26.8%, respectively. The microstructure variation was the main reason for the synchronous improvement in thermal conductivity and integrated mechanical properties. Especially, the morphology variation of the eutectic Si phases from flak to fiber could significantly improve the thermal conductivity and integrated mechanical properties.

1. Introduction
With the continuous development of new industries such as 5G communication and new energy vehicles, higher requirements have been placed on the thermal conductivity of important heat dissipation components (e.g., RRU sealed cavity housing and battery heat dissipation module). There are two basic methods to improve the heat dissipation performance of heat dissipating components. The first method is to improve the thermal conductivity of the material itself, and the other method is to optimize the component structure to improve the heat dissipation performance of the component. The former method is the basic premise. Among all metals and alloys, the thermal conductivity of aluminum is only inferior to that of Ag, Cu and Au, and the price of aluminum is much cheaper than the aforementioned materials. However, the mechanical properties of aluminum are very poor. In engineering applications, it is often necessary to improve the mechanical properties of Al alloys through alloying [1–6]. However, alloying would significantly reduce the thermal conductivity of Al alloys due to the negatively-correlated relationship between the mechanical properties and thermal conductivity of metal materials [4, 7]. But in engineering applications, there is a great need for cast Al alloys with both excellent thermal conductivity and mechanical properties. Therefore, how to obtain excellent thermal conductivity and mechanical properties by alloying at the same time is the main challenge for current research on high thermal conductivity Al alloys.

Die casting is the main molding method of Al alloys components with thin-walled heat-dissipating components. In casting Al alloys, Si is the most widely used alloying element, which can improve both the mechanical properties and casting properties of Al alloys. However, the thermal conductivity of Al alloys will be significantly reduced with the increase of Si content [7]. Accordingly, the Si content is the key to balance the mechanical properties and thermal conductivity in the development of cast high thermal conductivity Al alloys. A356 Al alloy is a widely used commercial alloy with a Si content of about 7%. A356 Al alloy exhibits good mechanical and casting properties but poor thermal conductivity [8]. In cast Al alloys, Fe is a commonly used alloying element. Fe can effectively suppress the sticking of Al alloys castings, and enhances casting demoulding...
property and production efficiency. In addition, Fe can effectively reduce the solid solubility of Si in Al matrix and thereby improve the thermal conductivity of Al–Si alloys [3, 4]. Zn could effectively improve the mechanical properties of Al alloys [5], and has a less negative effect on the thermal conductivity of Al alloys than Si and Fe [9]. Therefore, a proper amount of Fe and Zn is beneficial to optimize the thermal conductivity and mechanical properties of Al alloys. An Al–7Si–xFe–yZn alloy system with excellent thermal conductivity and high tensile strength has been developed in our previous research [8, 10].

In Al–7Si alloys system, the coarse flaky eutectic Si phase deteriorates the mechanical properties and thermal conductivity [4, 7, 11–14]. Sr could effectively change the morphology of eutectic Si phases from coarse flake to fine fiber in Al–Si alloys [1, 15–18]. Some scholars found that the change of Si phase morphology is beneficial to improve not only the electrical conductivity and thermal conductivity of Al alloys [15, 16, 18], but also the mechanical properties [1, 17]. Wen et al [18] found that the thermal conductivity of Al–7Si alloy was increased from 149.9 (W/m.K) to 169.6 (W/m.K) by addition of 0.05% Sr. Shin et al [1] proposed that the tensile strength of Al–10.5Si–2Cu alloy increased from 209 MPa to 237 MPa after being modified by Sr.

B can effectively improve the electrical conductivity of Al alloy, and is widely used in the development of high-strength cables of Al alloys [19–21]. In addition, it was reported that B could improve the electrical conductivity of cast Al–Si alloys. Wang et al [22] found that the electrical conductivity was increased by 12.8% after adding 0.06% B in A365 casting Al alloy. According to Weizmann–Frantz law [7, 14], the electrical conductivity of alloys is normally proportional to the thermal conductivity. Therefore, B also can improve the thermal conductivity of Al alloys. In addition, B can effectively refine the primary α-Al grains, and thereby improving the mechanical properties of Al alloys [6, 23, 24]. Accordingly, similar to Sr, B could also improve both the thermal conductivity and mechanical properties of Al–Si alloys.

Based on the above researches, it has great value to take advantage of B and Sr to compositely improve the thermal conductivity and mechanical properties of Al–Si alloys. However, some researches [25–28] found the co-poisoning effect between B and Sr in B/Sr composite modified Al–Si alloys, which could seriously deteriorate the modification effect of Sr on eutectic Si phases. Therefore, how to effectively inhibit the co-poisoning effect between B and Sr has been a crucial problem to address. Both Chen et al [29] and Li et al [30] found that La could be used as a neutralizing element in B/Sr composite modified Al–Si alloys. When these modifiers are added in melt in the order of B-La-Sr, the co-poisoning effect between Sr and B can be inhibited by La [29, 30]. However, in B/La/Sr composite modified Al–Si alloys, the influence of microstructure changes on thermal conductivity and mechanical properties has not been revealed. In addition, the effect of La content on the thermal conductivity and mechanical properties of B/La/Sr composite modified alloys is still unclear. These are worthy of in-depth study and analysis.

In this research, Al–7Si–0.6Fe–0.5Zn alloy was used as base alloy. The effect of B/La/Sr composite modification on the microstructure and solidification processes of base alloy would be analyzed in depth. The influence of modification processes on the thermal conductivity and mechanical properties of base alloy was also studied. This research will provide a valuable process reference for the development of Al–Si alloys with both excellent thermal conductivity and tensile strength.

2. Experimental procedures

The commercial pure Al (99.8% Al, 0.095% Fe, 0.035% Si, 0.02% Zn, etc) (mass ratio, the same below), pure Zn, Al–20Si and Al–20Fe master alloys were used as raw materials. Al–3B, Al–10Sr and Al–10La master alloys were used as modifiers. The base alloy (Al–7Si–0.6Fe–0.5Zn) was first smelted by use of raw materials, and then different modified alloys were prepared using the base alloy to ensure that the basic composition of all samples was the same. The modification processes of all modified alloys were shown in table 1. A total of 7 samples were prepared in this research, which were sequentially labeled No. 0 ~ No. 6, and No. 0 was marked as base alloy.

The raw materials were held in graphite clay crucible and melted in an electric resistance furnace (SG2-5-10). The melting temperature was set at 750 °C. For preparing B modified alloy or Sr modified alloy, the base alloy was completely melted first, and then the modifier was added to the melt and immediately stirred for 30 s. Subsequently, the melt was hold for ten minutes and cast finally. For preparing the composite modified alloy, the addition order of modifiers was shown in table 1. The modifiers were added to melt separately at intervals of ten minutes. In order to ensure homogenization, the melt was immediately stirred for 30 s after modifier being added. After adding the last modifier and holding for ten minutes, the melt was cast. The melt was poured into a steel mold preheated at 200 °C to obtain a casting with a thickness of 4 mm. The melt solidification rate was about 30 ~ 40 °C s⁻¹.

The as-cast samples were processed into cylinders (Ø12.7×3 mm) and then employed to determine the thermal diffusivity (α) by the laser flash method (NDT ZSCH DSC 204F1) at room temperature. The density (ρ) and heat flow value (Φ) were measured by density balance (GF300–D) and differential scanner (Netzsch DSC),
respectively. Each parameter was measured three times, the relative error of every data was less than 5%, and then averaged. The specific heat \( C_p \) was calculated by \( \Phi \). At last, the thermal conductivity \( \lambda \) of each alloy was calculated by the formula: \( \lambda = \alpha \rho C_p \). The morphology of primary \( \alpha \)–Al grains and iron-rich metal compound were observed by optical microscope. In order to observe the three-dimensional morphology of eutectic Si phases, the samples were deep-etched with 10% hydrochloric acid alcohol for 30 min, and then the surface of the samples were washed with absolute alcohol. The morphology of eutectic Si phases was observed by SEM-SEI (ZEISS Merlin). To analyze the solidification process, the solidification cooling curves of the alloys were measured by a temperature data acquisition instrument (NIT9212). After the raw material was completely melted, it was kept at 750 °C for 15 min. Subsequently, the crucible holding the melt was put into a self-made holding furnace. Lastly, the thermocouple was placed in the center of the melt, and the temperature was collected during solidification. The cooling rate of the melt was about 0.2 °C s^{-1}. The tensile test bars were tested by the universal testing machine (Shimadzu, AG-X Plus 100KN) at a constant extension rate of 1 mm min^{-1} at room temperature. The tensile samples were processed into sheets, and the cross-sectional dimensions of the tensile part are 6 mm × 3 mm. Three specimens were tested to get an average value of ultimate tensile strength \( \sigma_b \) abbreviated as UTS and elongation \( \delta \). The Q value was used as integrated mechanical properties index which combined both the \( \sigma_b \) and \( \delta \). The Q value is defined as: \( Q = \sigma_b + a \cdot \log(\delta) \). The \( a \) value is 150 MPa for Al-7Si alloys system [11, 31, 32].

3. Results

### 3.1. Thermal conductivity and ultimate tensile strength

The \( \rho \), \( \alpha \), \( C_p \), \( \lambda \), increment of \( \lambda (\Delta \lambda, \Delta \lambda = \lambda_{unmd} - \lambda_{unmd}) \) and increasing rate of \( \lambda (\Delta \lambda/\lambda_{unmd}) \) were listed in table 2. The contrast of thermal conductivity was shown in figure 1. For better to compare, the \( \sigma_b, \delta \), Q, increment of Q \( (\Delta Q) \) and increasing rate of \( Q (\Delta Q/\lambda_{unmd}) \) were also listed in table 2. The contrast of mechanical properties was shown in figure 2.

The figure 1(a) showed that thermal conductivity of base alloy (No. 0) was the lowest among all alloys, only 132.4 (W/(m·K)). Through different modification processes, the thermal conductivity of all modified alloys was improved by different degree, as shown in figure 1(b). In addition, it could be found from figure 1(b) and table 2 that the \( \Delta \lambda \) and \( \Delta \lambda/\lambda_{unmd} \) of all modified alloys had the following change laws.

The \( \Delta \lambda \) and \( \Delta \lambda/\lambda_{unmd} \) of B modified alloy (No. 1) were the smallest, only 6.3 (W/(m·K)) and 4.8% respectively. The \( \Delta \lambda \) and \( \Delta \lambda/\lambda_{unmd} \) (12.0 (W/(m·K)) and 9.1%) of B/Sr composite modified alloy (No. 3) were only higher than those (6.3 (W/(m·K)) and 4.8%) of B modified alloy (No. 1), but were far lower than those (29.7 (W/(m·K)) and 22.4%) of Sr modified alloy (No. 2). The \( \Delta \lambda \) and \( \Delta \lambda/\lambda_{unmd} \) (33.9 (W/(m·K)) and 25.6%) of B/0.15La/Sr composite modified alloy (No. 4) were the highest among all modified alloys. It was worth noting that \( \Delta \lambda/\lambda_{unmd} \) (25.6%) of B/0.15La/Sr composite modified alloy was close to the sum of that of B modified alloy (4.8%) and that of Sr modified alloy (22.47%). Additionally, with the increase of La content, the \( \Delta \lambda \) and \( \Delta \lambda/\lambda_{unmd} \) of B/La/Sr composite modified alloys (No. 4 ~No. 6) gradually decreased.

The tensile behaviour of five alloys (No. 0 ~ No. 4) were shown in figure 2(a). The curves in figure 2(a) showed that all alloys had no obvious yield point, while the modification processes had a significant effect on \( \sigma_b \) and \( \delta \). The figures 2(b)–(d) was drawn according to the data in table 2. The figure 2(b) showed that both the \( \sigma_b \) and \( \delta \) of all modified alloys were improved by different degree. Correspondingly, the Q was improved at the same time, as shown in figure 2(c). Since it was difficult to compare mechanical properties through \( \sigma_b \) and \( \delta \) at the same time, the Q which combined both the \( \sigma_b \) and \( \delta \) was used to analyze the changing laws of mechanical properties.

The Q (226.5 MPa) of base alloy (No. 0) was the least among all alloys, as shown in figure 2(c). Through different modification processes, the Q of all modified alloys was increased by different degree, as shown in

### Table 1. The modification scheme of Al–7Si–0.6Fe–0.5Zn alloy.

| Sample | B  | La | Sr  | Note                        |
|--------|----|----|-----|-----------------------------|
| No.0   | —  | —  | —   | Base alloy                  |
| No.1   | 0.1% | —  | —   | B modification              |
| No.2   | —  | —  | 0.1%| Sr modification             |
| No.3   | 0.1%| —  | 0.1%| B/Sr composite modification |
| No.4   | 0.1%| 0.15%| 0.1%| B/La/Sr composite modification |
| No.5   | 0.3%|    |     |                            |
| No.6   | 0.6%|    |     |                            |
Table 2. The thermal conductivity and mechanical properties of Al–7Si–0.6Fe–0.5Zn alloy modified by different processes.

| Sample | ρ (g cm⁻³) | α (mm² s⁻¹) | C_p (J/g K) | λ (W/(m·K)) | Δλ/λ_unmd (%) | σ_b (MPa) | δ (%) | Q (MPa) | ΔQ (MPa) | ΔQ/Q_unmd (%) |
|--------|------------|-------------|-------------|-------------|----------------|-----------|-------|---------|----------|----------------|
| No.0   | 2.661      | 62.69       | 0.7938      | 132.4 (λ_unmd) | —              | —         | 153.4 | 3.07    | 226.5    | (Q_unmd) |
| No.1   | 2.660      | 64.01       | 0.8148      | 138.7       | 6.3            | 4.8       | 178.8 | 4.81    | 281.1    | 54.6          |
| No.2   | 2.655      | 69.31       | 0.8807      | 162.1       | 29.7           | 22.4      | 194.4 | 6.25    | 313.8    | 87.5          |
| No.3   | 2.658      | 64.27       | 0.8453      | 144.4       | 12.0           | 9.1       | 183.4 | 5.43    | 293.6    | 67.1          |
| No.4   | 2.651      | 70.52       | 0.8893      | 166.3       | 33.9           | 25.6      | 191.4 | 7.68    | 324.2    | 97.7          |
| No.5   | 2.653      | 69.88       | 0.8853      | 164.1       | 31.7           | 23.9      | 185.6 | 6.24    | 304.9    | 78.4          |
| No.6   | 2.656      | 67.59       | 0.8864      | 159.1       | 26.7           | 20.2      | 183.1 | 5.11    | 289.4    | 62.9          |

Note: Δλ = λ_md - λ_unmd, ΔQ = Q_md - Q_unmd.

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Among all modified alloys, the $\Delta Q$ and $\Delta Q/Q_{\text{unmod}}$ of B modified alloy (No. 1) were the least, only 54.6 MPa and 24.1%. The $\Delta Q$ and $\Delta Q/Q_{\text{unmod}}$ (67.1 MPa and 29.6%) of B/Sr composite modified alloy (No. 3) were far lower than those (87.5 MPa and 38.6%) of Sr modified alloy (No. 2), but slightly higher than those (54.6 MPa and 24.1%) of B (No. 1) modified alloy. However, the $\Delta Q$ and $\Delta Q/Q_{\text{unmod}}$ (97.7 MPa and 43.1%) of B/0.15La/Sr composite modified alloy (No. 4) was the highest among all alloys. Additionally, the $\Delta Q$ and $\Delta Q/Q_{\text{unmod}}$ of B/
La/Sr composite modified alloys (No. 4 ~ No. 6) gradually decreased with the increase of La content. Compared with the $\sigma_b$ and $\delta$ of base alloy, the increasing rate of $\sigma_b$ and $\delta$ of B/0.15La/Sr composite modified alloy were 24.8% and 150%, respectively.

### 3.2. Microstructure

Figure 3 was the optical image of the microstructure of base alloy and modified alloys. The microstructure of all alloys was mainly composed of primary $\alpha$-Al and eutectic structure due to the small content of Fe and Zn.

Figure 3 showed that the morphology and dimension of the primary $\alpha$-Al grains of base alloy were significantly different with those of modified alloys. The length of primary dendrite (LPD) of primary $\alpha$-Al grains in each alloy was measured using Image-Pro plus software and the measurement results was summarized in table 3.

Figure 3(a) illustrated that the morphology of primary $\alpha$-Al grains was coarse columnar, and the maximum LPD of primary $\alpha$-Al grains was more than 2 mm in base alloy. The morphology and dimension of the primary $\alpha$-Al grains were changed by different degree with different modification processes. Figure 3(b) showed that the primary $\alpha$-Al grains were changed to fine equiaxed grains by B modification process, and the average LPD was reduced to 161.4 $\mu$m. Figure 3(c) showed that the primary $\alpha$-Al grains were changed to fine columnar grains by Sr modification process, and the maximum LPD was more than 2 mm. Figures 3(d) and (e) showed that the
primary α-Al grains in B/Sr and B/0.15La/Sr composite modified alloy were a mix structure of columnar and equiaxed grains, and the average LPD of primary α-Al grains in the two composite modified alloys was 180.1 μm and 185.4 μm, respectively. The morphology and dimension of the primary α-Al grains in the two composite modified alloys were approximately the same, and was significantly smaller than that of base alloy. Among all the modified alloys, the average LPD of B modified alloy was the smallest (161.4 μm).

In addition, figure 3 showed that there were much slender needle phases in all alloys, as shown by black arrows in the enlarged view of the white rectangular area. The phase was identified as iron-rich β phases (Al5SiFe) according to the morphology [33]. Accordingly, figure 3 showed that all of the modified processes did not effectively transform the morphology of β phases. In addition, the solid solubility of Zn in the α-Al matrix is high, so it was difficult to observe obvious Zn-rich phase in all alloys. For B/La/Sr composite modified alloys, there was no obvious difference in the optical image of microstructure, so only the optical image of B/0.15La/Sr composite modified alloy was given in figure 3.

The morphology of eutectic Si phases in each alloy was illustrated in figure 4. Apparently, the morphology of eutectic Si phases in base alloy was coarse flake, and the maximum length exceeded 30 μm. Compared with the basic alloy, the morphology and dimension of the eutectic Si phases were not changed in B modified alloy, as shown in figure 4(b). Figure 3(c) showed that most of the eutectic Si phases were fine fibrous structure, and only a small amount of them were flaky structure (as shown by white arrow) in Sr modified alloy. In B/Sr composite modified alloy, most of eutectic Si phases were in the form of flake, and the maximum length of eutectic Si phases exceeded 30 μm, as shown in figure 4(c). In addition, there were a small amount of short-fine fibrous eutectic Si phases in figure 4(d) (as shown by white arrow), but the proportion was much smaller than that of flakey eutectic Si phases. In B/0.15La/Sr composite modified alloy, most of eutectic Si phases were fine fibrous structure, and the circular diameter of them was similar with that of Sr modified alloy, about 0.2–0.5 μm. In addition, there was a small amount of flaky eutectic Si phases in B/0.15La/Sr composite modified alloy, as shown by white arrow in figure 4(e). That is to say, the morphology of the eutectic Si phases in B/0.15La/Sr composite modified alloy was similar to that of Sr modified alloy, and was obviously different with that of the B/Sr composite modified alloy.

For B/La/Sr composite modified alloys, there was no obvious difference in the morphology of eutectic Si phases, so only the SEM image of B/0.15La/Sr modified alloy was given in figure 4. The morphology of eutectic Si phases of all alloys in figure 4 was summarized in table 3.

### 3.3. Thermal analysis

To analyze the microstructure evolution of all alloys, the cooling curves of all alloys were obtained by thermal analysis, and the first derivative curves was obtained by calculating the time derivative of cooling curve, as shown in figure 5. Similar methods were extensively employed in the solidification analysis of Al alloys [34–37]. For B/La/Sr composite modified alloys, there was no obvious difference in the cooling curves, so only the cooling curves of B/0.15La/Sr modified alloy was given in figure 5.

There were four peaks (indicated by arrows 1, 2, 3 and 4) in the first derivative curve of all alloys in figure 5. Every peak was related with a solidification reaction. According to the phase diagram of Al–Si alloys [38] and related literature [35, 36], the four peaks corresponded to primary α-Al solidification reaction (peak 1), (α-Al+β (Al5SiFe)) binary eutectic reaction (peak 2), (α-Al+Si) eutectic reaction (peak 3) and (α-Al+Si+β(Al5SiFe)) ternary eutectic reaction (peak 4). The above mentioned four solidification reactions were shown as follows:

\[
L \rightarrow \alpha - Al \\
L \rightarrow \alpha - Al + \beta \\
L \rightarrow \alpha - Al + Si \\
L \rightarrow \alpha - Al + Si + \beta
\]
Because of the small content of modified element, no obvious peak of secondary phase containing modified elements was found in first derivative curves of all modified alloys. However, it was found that the characteristic temperatures of eutectic solidification of some modified alloys were quite different with those of base alloy. The cooling curves of the eutectic solidification stage of base alloy and some modified alloys were shown in figure 5(f). The growth temperature ($T_G$) of base alloy, Sr modified alloy, B/Sr composite modified alloy and B/0.15La/Sr composite modified alloy was 574.84 °C, 571.84 °C, 574.74 °C and 572.95 °C, respectively. The $T_G$ of the three modified alloys was lower than that of base alloy, and the difference of $T_G$ ($\Delta T_G$, $\Delta T_G = T_G (\text{unmod}) - T_G (\text{md})$) was 3.00 °C, 0.10 °C and 1.89 °C, respectively.

4. Discussions

The experimental data showed that the modification processes significantly translate the morphology of microstructure. Meanwhile, the thermal conductivity and mechanical properties of these modified alloys were both improved by different degrees. Therefore, there was a close relationship between the change of microstructure morphology and the synchronous improvement in thermal conductivity and mechanical properties.
4.1. Microstructure

Compared with the base alloy, the LPD of B modified alloy was significantly refined to 161 μm, as shown in figures 3(a) and (b). Some studies [6, 23, 24, 28] also found that B can effectively refine primary α-Al grains. Liu et al [23] and Chen et al [24] found that an amount of AlB2 particles would be precipitated in the melt when B was added in Al–Si alloys, and AlB2 particles could act as nucleation substrate of primary α-Al grains.

Sr could significantly translate the morphology of eutectic Si phases from coarse flake to fine fibrous structure. This is because Sr could change the growth mechanism of eutectic Si phases. Before modification, the growth mechanism of eutectic Si phases is ‘twin plane reentrant edge’ (TPRE) mechanism [39, 40]. After modification by Sr, the growth mechanism of most of eutectic Si phases is changed to restriction of TPRE mechanism and ‘impurity induced twinning’ (IIT) mechanism, which translate the morphology of most of eutectic Si phases from coarse flake into fine fiber [39, 40].

For B/Sr composite modification process, i.e., the addition of B in Sr modified alloy, the co-poisoning effect between B and Sr would occur in melt [26, 29, 30]. As a result, in the melt, the freely available Sr and B to modify the microstructure were significantly reduced. Therefore, the modification effect of Sr on the eutectic Si phases would be significantly suppressed, and the morphology of most of the eutectic Si phases was reverted into flake instead of fine fiber [26, 29, 30]. Similarly, the modified effect of B on primary α-Al grains would also be suppressed, and the primary α-Al grains were deteriorated into a mix structure of columnar and equiaxed grains [26, 29, 30]. As a result, the LPD of B/Sr composite modified alloy was larger than that of B modified alloy, but still smaller than those of base alloy.

Figure 5. The thermal analysis curve: (a) base alloy, (b) Sr modified alloy, (c) B modified alloy, (d) B/Sr composite modified alloy, (e) B/0.15La/Sr composite modified alloy, (f) eutectic solidification cooling curves of four alloys (No. 0, No. 2 ~ 4).
For B/La/Sr composite modification process, i.e., the addition of La in the B/Sr composite modified alloys, the interaction between modifiers was more complicated. Some researches [29, 30, 41] found that La can effectively suppress the co-poisoning effect between B and Sr when the modifiers were added to the melt in the order of B-La-Sr; When La was added into the melt prior to Sr, the LaB6 was precipitated in the reaction between B and La [29, 30, 41]. As a result, the content of B in melt would be decreased. Subsequently, the last added Sr could maintain a higher concentration in the melt than that of B/Sr composite modified alloy, and therefore Sr could effectively modify eutectic Si phases. Accordingly, most of eutectic Si phases would be precipitated in the form of fiber instead of flake [27, 30]. Similar with AlB2, LaB6 could also be served as the heterogeneous nucleation substrate of primary α-Al grains, and thereby refining the primary α-Al grains [42, 43]. Given the same B, the amount of LaB6 precipitated in B/La/Sr composite modified alloy would be less than that of AlB2 precipitated in B modified alloy. As a result, the modified effect on the primary α-Al grains in B/0.15La/Sr composite modified alloy would be weaker than that of B modified alloy. Therefore, the primary α-Al grains in B/0.15La/Sr composite modified alloy would also be deteriorated into a mix of columnar and equiaxed grains [29, 30]. Consequently, the LPD was larger than that of B modified alloy, but still smaller than those of base alloy, just like that of B/Sr composite modified alloy. In addition, most of the remaining La in the melt would be precipitated in the form of metal compounds. Some researches [2, 44–47] found that in Al–Si alloy, La would react with Al and Si to form La-rich ternary metal compounds which were precipitated at grain boundaries.

The above analysis indicated that the difference of Sr concentration in melt was the main reason for the difference in the morphology of eutectic Si phases. For a given Si content, when the Sr content reached a critical value, the eutectic Si phases could be effectively modified. Vandersluis et al. [15] found that in A319 Al alloy, as long as the content of Sr was more than 154ppm, the eutectic Si phases could be modified. In addition, some researches [34, 48, 49] found that the Al–Si eutectic growth temperature (\(T_{G}\)) would be significant depressed in Al–Si alloys by Sr modification process. Djurdjevic et al. [49] studied the relationship between the content of Sr and the depression of eutectic growth temperature (\(\Delta T_{G} = T_{G}(\text{anneal}) - T_{G}(\text{md})\)) in A319 alloy, and found that the \(\Delta T_{G}\) was increased with Sr content increasing. The data of thermal analysis in this research confirmed the above analysis.

The \(T_{G}\) of Sr modified alloy, B/Sr modified alloy and B/0.15La/Sr modified alloy was all lower than that of base alloy. For Sr modified alloy, the \(\Delta T_{G}\) was 3.00 °C, which was the highest among all three modified alloys. This indicated that the Sr concentration was the highest in Sr modified alloy melt during eutectic solidification. However, the \(\Delta T_{G}\) of B/Sr composite modified alloy was only 0.2 °C, which was the lowest among all three modified alloys. This indicated that B would interact with Sr and significantly reduced the Sr concentration in melt. The \(\Delta T_{G}\) of B/0.15La/Sr composite modified alloy was 1.89 °C, which was slightly lower than that of Sr modified alloy, but was much higher than that of B/Sr composite modified alloy. This indicated that the La could significantly suppress the co-poisoning effect between B and Sr, and effectively maintain the Sr concentration in melt during the eutectic reaction.

### 4.2. Thermal conductivity and mechanical properties

From the analysis of 4.1, it could be seen that the microstructure of alloy had changed significantly by modification processes. This change would produce a direct impact on thermal conductivity and mechanical properties.

Some researchers [50–53] found that the interface between matrix and secondary phase can scatter free electrons and shorten the average free path of electrons. The cross-section dimensions of secondary phase significantly affect the electrical resistivity (\(\rho\)) of alloys, and the electrical resistivity (\(\rho\)) increases with the increase of \(P/S\) [51–53]. \(P\) and \(S\) refer to the perimeter and the cross-section area of secondary phase, respectively. According to Weizmann–Frantz law [7, 14], the electrical conductivity is normally proportional to the thermal conductivity of alloys. From the mentioned finding, it could speculate that in the given Si content, the increment of thermal conductivity should be improved by the proportion decreasing of flaky eutectic Si phases, since the \(P/S\) of rectangle cross-section of flaky eutectic Si phase is higher than that of the circular cross-section of fibrous eutectic Si phase. This speculation was confirmed by the experiment results of this study.

Since the eutectic Si phases had the largest fraction of all secondary phases in microstructure, it was a logically inferred that the change of the morphology of eutectic Si phases lead to the change of thermal conductivity. In Sr modified alloy, most of eutectic Si phases changed from coarse flaky structure to fine fibrous structure. Therefore, the thermal conductivity of Sr modified alloy was mainly improved by the morphology variation of eutectic Si phases. In addition, Vandersluis et al. [15] found that the morphology variation of eutectic Si phases from flake to fibrous could effectively improve the thermal conductivity of alloys.

Since B cannot effectively modify the eutectic Si phases, the mechanism of improving the thermal conductivity of B modified alloy was fundamentally different from that of Sr modified alloy. Some researches...
[19–21] found that B can effectively reduce the content of Zr, Ti, Cr and V in Al alloys, and these elements have a significantly adverse effect on thermal conductivity and electrical conductivity of Al alloys [19, 20, 54]. In this research, the industrial grade raw materials contain a trace of impurity elements (e.g., Zr, Ti, Cr and V). Therefore, the thermal conductivity of B modified alloy was improved by reducing the content of impurity elements.

In B/Sr composite modified alloy, B was added to the melt prior to Sr, and the impurity elements were firstly removed by B. The subsequent addition of Sr would co-toxin with the remaining B in melt, and consequently led to the precipitation of flake eutectic Si phases [26, 29, 30]. Although there were a small amount of fibrous eutectic Si phases in B/Sr composite modified alloy, the improvement of thermal conductivity by a small amount of fibrous eutectic Si phases was suppressed by most of flaky eutectic Si phases. Therefore, the thermal conductivity of B/Sr composite modified alloy was significantly lower than that of Sr modified alloy, and only slightly higher than that of B modified alloy.

In B/La/Sr composite modified alloys, the first addition of B could effectively reduce the content of impurity elements in melt. The addition of La could suppress the co-toxin effect between B and Sr, which effectively prompted Sr to translate the morphology of eutectic Si phases from flake into fiber [29, 30]. From the above analysis, it could be inferred that\(\Delta \lambda/\lambda_{\text{numa}}\) of B/La/Sr composite modified alloys should be close to the sum of that of B modified alloy and that of Sr modified alloy. However, the La-rich metal compounds would be precipitated in the form of flame [2, 45, 47], which would increase the scattering area of free electrons and reduce the thermal conductivity of modified alloy. As a result, \(\Delta \lambda/\lambda_{\text{numa}}\) of B/La/Sr composite modified alloys was slightly lower than the sum of that of B modified alloy and that of Sr modified alloy. The precipitation amount of La-rich metal compounds was increased with La content increasing, and thereby decreasing the thermal conductivity of B/La/Sr composite modified alloy. Since the content of La in B/0.15La/Sr composite modified alloy was the least among the three B/La/Sr composite modified alloys (No. 4 ~ 6), \(\Delta \lambda/\lambda_{\text{numa}}\) of B/0.15La/Sr composite modified alloy was the highest.

Besides, some studies found that the porosity was increased in Sr modified Al alloys. Vandersluis et al [15] found that the porosity was decreased with increasing cooling rate when 0.03% Sr modified B319 Al alloy. When the cooling rate was 5.9 °C s\(^{-1}\), the porosity of modified alloy was only about 0.2% higher than that of unmodified alloy. Since the cooling rate in this research was much higher than 5.9 °C s\(^{-1}\), it could be judged that the porosity in each alloy was not much different. Therefore, the effect of porosity on the thermal conductivity of different alloy was negligible. Additionally, the solid solubility of Sr in \(\alpha\)-Al was very low, and it is difficult for Sr to effectively change the solubility of Si in \(\alpha\)-Al in the as-cast state [50]. Therefore, it was very difficult for Sr to affect the thermal conductivity of the alloy by changing its own actual solid solubility in \(\alpha\)-Al or by changing the actual solid solubility of Si in \(\alpha\)-Al [50]. Due to the similar flaky structure of \(\beta\) (Al\(_3\)SiFe) phase in all modified alloys and base alloy, the thermal conductivity improvement of modified alloys was not related to the morphology of \(\beta\) phase.

The coarse dendritic structures and coarse flaky eutectic Si phases were the main components of the base alloy microstructure, which significantly limited the mechanical properties [11–13]. Therefore, the integrated mechanical properties of base alloys were the least among all alloys. So both refinement of primary \(\alpha\)-Al grains and transformation of eutectic Si phase morphology were beneficial to improve the integrated mechanical properties. Some researchers found that the introduction of B into melts was the effective way to achieve small uniformly distributed equiaxed grains, which improved the mechanical properties [6, 23, 24]. The mechanism of improving mechanical properties could be explained by the Hall-Petch equation [55, 56], i.e., the mechanical properties increased as the grain decreased. Other scholars found that the addition of Sr increases the UTS and elongation of the hypo-eutectic Al-Si alloys due to the refinement eutectic Si particles from a long, needle-like morphology to a fine, fibrous form [1, 17]. The mechanism of improving mechanical properties is that the fibrous eutectic Si phase could effectively reduce the cutting effect on the Al matrix [1, 17].

From the above analysis, it could be seen that the reason of improving the integrated mechanical properties of B-modified alloy and Sr-modified alloy in this study was very different. By comparison, the integrated mechanical properties of Sr modified alloy were higher than those of B modified alloy, indicating that the fibrous eutectic Si phase could improve the integrated mechanical properties more effectively than the refinement of primary \(\alpha\)-Al. This speculation could be verified on the integrated mechanical properties comparison of composite modified alloys.

The morphology and dimension of primary \(\alpha\)-Al in B/0.15La/Sr composite modified alloy and B/Sr composite modified alloy were very similar, while the morphology of eutectic Si phase was significantly differently in the two composite modified alloys. By comparison through table 2 and figure 2(d), the integrated mechanical properties (Q value) of the former were significantly higher than those of the later. This result confirms the above speculation.

In addition, though the morphology of the eutectic Si phases was the same, the LPD of primary \(\alpha\)-Al in B/0.15La/Sr composite modified alloy was significantly smaller than that of Sr modified alloy. Therefore, the
integrated mechanical properties of B/0.15La/Sr composite modified alloy were higher than those of Sr modified alloy, and were the highest among all alloys in this study. Additionally, La-rich brittle metal compounds were precipitated in the form of fine flaky, which significantly deteriorated the mechanical properties [2, 44–47]. Therefore, the integrated mechanical properties of B/Sr composite modified alloys gradually decreased with La content increasing.

Comparing the microstructure, $\Delta \lambda / \lambda_{\text{unmodified}}$ and integrated mechanical properties of all modified alloys, it could be found that the fibrous eutectic Si phases produced significant synchronous improvement in thermal conductivity and integrated mechanical properties. For example, the synchronous improvement of Sr modified alloy and B/0.15La/Sr composite modified alloy was significantly better than that of B modified alloy and B/Sr composite modified alloy.

In addition, in B/0.15La/Sr composite modified alloy, B could modify primary $\alpha$-Al and reduce impurity, and Sr could modify eutectic Si phase. Thus, the synchronous improvement effect of B/0.15La/Sr composite modified alloy was the best. However, the precipitation of La-rich metal compounds would produce an adverse effect on thermal conductivity and mechanical properties. Accordingly, for synchronous improvement in thermal conductivity and integrated mechanical properties of B/La/Sr composite modified alloys, the content of La is very critical.

5. Conclusions

(1) Different modification processes could synchronously improve the thermal conductivity and mechanical properties of base alloy by different degree. The synchronous improvement effect on B/Sr composite modified alloy was significantly lower than that of Sr modified alloy, and only slightly higher than that of B modified alloy.

(2) The synchronous improvement effect on B/0.15La/Sr composite modified alloy was the best among all modified alloys. The increasing rate of $\lambda$, $\tau_b$, $\delta$ and $Q$ were 25.6%, 26.8%, 150.2% and 43.1%, respectively, and then the synchronous improvement effect was deteriorated by increasing La content.

(3) The morphology variation of microstructure was the main reason for the synchronous improvement in thermal conductivity and integrated mechanical properties of modified alloys. Especially, the morphology variation of eutectic Si phases from flaky structure to fibrous structure significantly improved the thermal conductivity and mechanical properties at the same time.

(4) The deterioration of the synchronous improvement effect on B/Sr composite modified alloy was the co-poisoning effect between B and Sr. The reason of the most significantly synchronous improvement effect on B/0.15La/Sr composite modified alloy was that La could suppress the co-poisoning effect between B and Sr.

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