Article

Morphological Evolution of TiB<sub>2</sub> and TiAl<sub>3</sub> in Al–Ti–B Master Alloy Using Different Ti Adding Routes

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Abstract: Three different Ti addition routes were used to prepare an Al–5Ti–B Master Alloy: the halide salt route, the Ti-sponge route, and the partial Ti-sponge route. In the halide salt route, the raw materials were Al + KBF<sub>4</sub> + K<sub>2</sub>TiF<sub>6</sub>; K<sub>2</sub>TiF<sub>6</sub> was completely replaced by pure titanium for the Ti-sponge route versus the halide salt route; in the partial Ti-sponge route, K<sub>2</sub>TiF<sub>6</sub> was partially replaced by pure titanium. Here, 30% Ti-sponge or 60% Ti-sponge route means that 30% or 60% K<sub>2</sub>TiF<sub>6</sub> was replaced by pure titanium, respectively. The above Ti addition routes have a significant influence on the growth pattern and morphological evolution of TiAl<sub>3</sub> and TiB<sub>2</sub>, which greatly affect the refining performance of Al–Ti–B Master Alloy. When using the halide salt route, a streamlined “rich Ti, B area” exists in the aluminum melt, which is a complex compound of (Ti<sub>x</sub>, Al<sub>1−x</sub>) B<sub>y</sub>. The “rich Ti, B area” is essential for the nucleation and growth of TiAl<sub>3</sub> and TiB<sub>2</sub>. Blocky TiAl<sub>3</sub> was obtained and its average size was 4.7 μm based on the halide salt route. In the Ti-sponge route, the nucleation of TiAl<sub>3</sub> mainly depends on the mutual diffusion of Al and Ti, and TiAl<sub>3</sub> forms around pure Ti particles, i.e., the so-called Ti–TiAl<sub>3</sub> mechanism. The average size of the blocky TiAl<sub>3</sub> was 9.8 μm based on the Ti–TiAl<sub>3</sub> mechanism. For the partial Ti-sponge route, the “rich Ti, B area” gradually decreases with the increase in Ti powder’s contents, and large TiAl<sub>3</sub> coexists with the small TiAl<sub>3</sub>. Compared with the Ti-sponge route, the halide salt route can form smaller TiAl<sub>3</sub>. In the Ti-sponge route, there is a small amount of “rich Ti, B area” due to the influence of the Ti–TiAl<sub>3</sub> mechanism, which does not meet the requirements of TiB<sub>2</sub> growth. In the halide salt route, there is sufficient “rich Ti, B area”, which is conducive to the formation of TiB<sub>2</sub>. Both the crystal defects and the crowded growth environment caused by the “rich Ti, B area” are fundamental reasons for the fragility and the irregular shape of the TiB<sub>2</sub>. The refining effect of the Al–Ti–B Master Alloy prepared by the halide salt route is better than the Ti-sponge route. The refining effect of 30% Ti-sponge route is better than that of Ti-sponge route and worse than that of halide salt route.

Keywords: Al–Ti–B Master Alloy; TiB<sub>2</sub>; TiAl<sub>3</sub>; halide salt route; “Ti-sponge” route; “partial Ti-sponge” route; Ti–TiAl<sub>3</sub> mechanism

1. Introduction

Al–Ti–B Master Alloy is an essential grain refiner and can strongly refine the microstructure and prevent the formation of coarse and equiaxed grains as well as columnar grains during the casting process of aluminum and aluminum alloy. It can also make the ingot’s microstructure become uniform, reduce segregation, and inhibit cracks. This greatly improves the mechanical and physical properties of aluminum and aluminum alloys [1–5]. The refinement mechanisms of Al–Ti–B Master Alloy are complicated and mainly include carbide–boride particle theory [6], peritectic reaction theory [7], peritectic hulk theory [8], and the duplex nucleation mechanism [9]. Of these, the duplex nucleation theory has
attracted extensive attention [10]. The theory shows that after the Al–Ti–B was added into the aluminum melt, the melting of TiAl 3 releases Ti. Ti then segregates toward TiB 2 surface, which leads to an increase in the Ti concentration around TiB 2 and formation of TiAl 3 outside of TiB 2. In this theory, the TiB 2 phase plays an indirect nucleation role. The duplex nucleation mechanism indicates that a smaller size of TiB 2 and TiAl 3 leads to a more uniform distribution of the second phase—this in turn leads to better refining of the Al–Ti–B Master Alloy.

The preparation methods of Al–Ti–B mainly include the halide salt route [11,12], the Ti-sponge route [13], the self-propagating high-temperature synthesis method [14,15], and the reprecipitated TiB 2 particles method [16]. The halide salt route and the Ti-sponge route are the primary methods for preparing. The halide salt route adds K 2 TiF 6 and KBF 4 into the aluminum melt according to the Ti/B value of the required product. The related reactions during the halide salt route are shown in Formulas (1)–(3) [17]. It is low-cost, simple production equipment and offers continuous production of stable and efficient refining effects for Al–Ti–B [13,18]. The Ti-sponge route replaces the K 2 TiF 6 in the halide salt route with Ti powder, as shown in Formulas (4) and (5) [19]. The formation and evolution mechanisms of TiAl 3 and TiB 2 are different for the halide salt route and the Ti-sponge route.

\[
6\text{KBF}_4(l) + 3\text{K}_2\text{TiF}_6(l) + 10\text{Al}(l) \rightarrow 3\text{TiB}_2(s) + 9\text{KAlF}_4(l) + 3\text{K}_3\text{AlF}_6(l) \quad (1)
\]

\[
3\text{K}_2\text{TiF}_4(l) + 13\text{Al}(l) \rightarrow 3\text{TiAl}_3(s) + 3\text{KAlF}_4(l) + 3\text{K}_2\text{AlF}_6(l) \quad (2)
\]

\[
2\text{KBF}_4(l) + 3\text{Al}(l) \rightarrow \text{AlB}_2(s) + 2\text{KAlF}_4(l) \quad (3)
\]

\[
2\text{KBF}_4(l) + 2\text{Ti} + 5\text{Al}(l) \rightarrow \text{TiB}_2(s) + \text{TiAl}_3(s) + 2\text{KAlF}_4(l) \quad (4)
\]

\[
2\text{KBF}_4(l) + 3\text{Al}(l) \rightarrow \text{AlB}_2(s) + 2\text{KAlF}_4(l) \quad (5)
\]

Liu [20] studied the relationship between the morphology of TiAl 3 and the smelting temperature for the halide salt route. Low-temperature smelting can form block-shaped TiAl 3 , while high-temperature smelting can quickly form rod-shaped TiAl 3 crystals. Xie [21] also found that TiAl 3 mainly has two morphologies: block-shaped and rod-shaped; the solute Ti grows easily around the agglomerate TiAl 3 , and TiB 2 also has specific morphological evolution. TiB 2 particles are hexagonal and independent when Al–Ti–B Master Alloy was prepared by the halide salt route [22]. The reaction temperature does not influence the morphology of TiB 2. However, TiB 2 particles showed different morphologies at different reaction temperatures when the Master Alloy was prepared by the Ti-sponge route [12]. The TiB 2 particles are larger than 5 µm when the reaction temperature is 850 °C. When the reaction temperature reached 1200 °C, TiB 2 particles gradually changed into layered stacking morphology and even a dendritic morphology. Zhang [23] confirmed by kinetic analysis that TiB 2 particles are not stable in Al melt and Ti addition can suppress the dissolution of TiB 2 particles. TiB 2 may coarsen during the holding temperature and grow during the cooling of the melt. Wang [24] demonstrates a strong epitaxial growth of TiAl 3 on the surface of TiB 2 particles. Fan et al. also found that a layer of TiAl 3 was formed on the surface of TiB 2 and that TiAl 3 can significantly improve the stability of TiB 2 [25]. TiAl 3 and TiB 2 also interact with each other. Wang et al. also proved that TiB 2 is critical to grain refinement of aluminum and aluminum alloys [26]. TiB 2 particles react with aluminum slowly and release Ti into the melt. The TiAl 3 particles then combine with Ti in the melt to form a dynamic Ti-rich layer on the surface of (Ti, Al) B 2. This layer offers a low crystal mismatch with α-Al and promotes the nucleation of aluminum grains.

The Ti-sponge route replaces K 2 TiF 6 in the halide salt route with Ti powder. According to the addition amount of raw materials, the amount of K 2 TiF 6 needed, for the same content of Ti, is five times that of Ti powder. The preparation of 1 ton of Al–5Ti–B master alloy needs 0.3665 tons of mixed fluoride salt of K 2 TiF 6 and KBF 4 but only 0.1665 tons of Ti powder and KBF 4. The liquid salt slags and fluoride gas produced by Ti-sponge route are much lower than that of the halide salt route. Therefore, the fluoride pollution of halide salt route is much more serious than that of the Ti-sponge route. The partial Ti-sponge
route of combining the halide salt route and the Ti-sponge route may have a better refining effect and improved environmental effects. It is necessary to explore the refining effect of Al–Ti–B Master Alloy using different Ti adding routes.

The growth pattern and morphology distribution of the TiAl₃ and TiB₂ for different preparation processes have not been thoroughly studied. The difference between the Ti-sponge route and halide salt route is quite rarely analyzed. Here, an Al–Ti–B Master Alloy was prepared using different Ti addition routes including the halide salt route, the Ti-sponge route, and the partial Ti-sponge route. The growth pattern and morphological evolution of the TiAl₃ and TiB₂ were analyzed, and the refining effects using different Ti adding routes were also discussed.

2. Experimental

Table 1 shows the experimental parameters of Al–5Ti–B Master Alloy prepared by the halide salt route. Pure aluminum, KBF₄, and K₂TiF₆ were all added at a nominal composition of the Al–5Ti–B Master Alloy (Al:Ti:B = 100:12.4:26.6, weight ratio). The dried pure aluminum was heated to 800 °C in a graphite crucible until the metal was soft-crushed. A coating agent (10.8% calcium fluoride + 72.8% magnesium chloride + 16.4% chlorinated calcium) was then covered on the surface of the aluminum melt. The slag was removed after a hexachloroethane refiner was added at 720 °C and held for 1200 S. When increasing temperature to the experimental reaction temperature (Table 1), mixed fluoride salt (KBF₄ and K₂TiF₆ were premixed before adding) was added into the aluminum melt, stirred evenly, and held for 10–1800 S (Table 1). The melt was then poured into a preheated steel mold to obtain a cubic ingot (160 × 100 × 12 mm).

Table 1. Experiment parameters for Al–5Ti–B Master Alloy prepared by the halide salt route.

| Temperature  | Reaction Time |
|--------------|---------------|
| 800 °C       | 10 S          |
|              | 15 S          |
|              | 20 S          |
|              | 30 S          |
|              | 60 S          |
|              | 300 S         |
|              | 600 S         |
|              | 1800 S        |

Table 2 shows the experimental parameters of Al–5Ti–B Master Alloy prepared by the partial Ti-sponge route and Ti-sponge route. Based on the halide salt route, K₂TiF₆ was gradually replaced by pure Ti. The Ti-sponge route means that K₂TiF₆ was totally replaced by pure Ti. The 30% Ti-sponge route and 60% Ti-sponge route mean that K₂TiF₆ was partially replaced by 30% Ti and 60% Ti, respectively.

Table 2. Experimental parameters for the partial Ti-sponge route and the Ti-sponge route.

| Content of Ti     | Reaction Time |
|-------------------|---------------|
| 30% Ti-sponge route | 15 S          |
| 60% Ti-sponge route | 300 S         |
| Ti-sponge route     | 1800 S        |

The microstructure samples were cut from the center of the ingots at the center height, mounted, and mechanically polished. The samples were then etched using Keller’s reagent for 10 s. The microstructures were characterized using a Leica DMR research optical microscope (OM) and a SU-8020 field emission gun scanning electron microscope (FEG SEM) operating at 45 kV and a tube current of 40 µA. A D/max 2500V X-ray diffractometer equipped with Ni-filtered Cu Kα radiation source scanning over a range of 2θ = 20–80° was used to analyze TiB₂ and TiAl₃.

3. Results

3.1. “Rich Ti, B Area” and Morphology of TiAl₃, TiB₂ in Halide Salt Route

The possible reactions during the Al–Ti–B Master Alloys prepared by the halide salt route are shown in Formulas (1)–(3). These reactions are the main sources of TiAl₃ and
TiB₂. Figure 1 shows the microstructure and composition of Al–Ti–B prepared by the halide salt route at 800 °C with different reaction times. There are obvious filamentous areas in Figure 1a. According to the EDS analysis, the filamentous areas were rich in elemental Ti but did not contain element F. This indicates that these areas should be the product areas of the fluoride salt reaction. The ratio of Ti to Al at point 2 is about 34.6%, which is nearly equal to the mass fraction of Ti in TiAl₃ (about 36.96%). Considering that Al may be oxidized, point 2 should be TiAl₃. Point 1 contains Ti and the energy spectrometer cannot detect the existence of B; therefore, we infer that the filamentous area is at least rich in Ti. The filamentous area gradually disappeared with longer reaction times. The filamentous area greatly reduced at 30 S (Figure 1b), and TiAl₃ of thin rods or small blocks and aggregative TiB₂ appeared. The filamentous area disappeared at 60 S (Figure 1c). At this point, the TiAl₃ became thick rods and large blocks, and TiB₂ dispersed into coarse grains. When the reaction time was extended to 600 s, the TiB₂ further dispersed into fine particles (Figure 1d), thus distributing in the Al matrix. TiB₂ was generated in the incipient filamentous area, which suggests that the filamentous Ti-rich area was also rich in B. Therefore, the filamentous area should be called the “rich Ti, B area”.

![Figure 1. Microstructure and EDS of Al–Ti–B Master Alloy prepared by the halide salt route with different reaction times at 800 °C. (a) 10 S; (b) 30 S; (c) 60 S; (d) 600 S.](image)

The XRD spectra at 800 °C for different reaction times are shown in Figure 2 to further confirm the “rich Ti, B area”. The main phases of all samples were Al, TiAl₃, and TiB₂, and no prominent excess peaks were observed. The intensity of the TiAl₃ peak is basically the same from 10 S to 1800 S, which indicates that TiAl₃ generated at the initial stage of the halide salt reaction. The TiB₂ peak obviously changed from weak to strong. There is no TiB₂ peak in the XRD pattern at 10 S and a weak TiB₂ peak appears at 15 S, thus...
indicating that the formation of TiB$_2$ is slower than that of TiAl$_3$ or it generates too little to detect in the early stage. The TiB$_2$ and AlB$_2$ have a similar crystal structure, and thus, diffraction peaks may be broadened or separated in XRD diffraction. If the value of Ti/B is greater than 2.2, then excess B will form AlB$_2$ [27]. Therefore, the peaks in the two square frames in Area1 were considered to be AlB$_2$, which are very close to the strong peak of TiB$_2$. A small amount of AlB$_2$ also exists in the early stage of the reaction. Some studies have reported the nonhomogenous distribution of solutes B and Ti close to the salts/Al melt interface during the reaction of the fluoride salts and Al melt. These form unstable AlB$_2$. The AlB$_2$ transforms to TiB$_2$ via diffusion of solutes Ti and B in the aluminum melt in the subsequent holding temperature process [28,29]. The essence of filamentous areas (Figure 1a) is a complex compound (Ti$_x$Al$_{1-x}$)$_y$; this area was called the “rich Ti, B area". In the early stage of the halide salt reaction, the streamlined “rich Ti, B area" existed in the aluminum melt (Figure 1a). The formation of TiAl$_3$ was very fast (less than 10 S). The “rich Ti, B area" was the birthplace of the nucleation and growth of initial TiAl$_3$ and TiB$_2$ for the halide salt route.

Figure 2. XRD pattern of Al–Ti–B Master Alloy prepared by the halide salt route at 800 °C for different reaction times.

Figure 3 clearly shows the morphology of the TiB$_2$ in the Al–Ti–B Master Alloy prepared by the halide salt route at 800 °C for 300 S. The white shadow on the particle’s edge shows that TiB$_2$ is hexagonal with a certain thickness. The maximum section size of these...
hexagons is 0.5–1.0 µm. In the statistics of T.E. Quested [28], the size of TiB₂ particles in conventional Al–Ti–B Master Alloy is about 5 µm, and the size of most TiB₂ is 0.5–1.5 µm. Figure 3b shows the irregular TiB₂; they may be the side cuts of the hexagonal TiB₂; however, the mutual “crashing” during fragile TiB₂’s growth also may lead to the forming of the irregular shape (Figure 3c).

![Figure 3](image1)

**Figure 3.** Morphology of TiB₂ in the Al–Ti–B Master Alloy prepared by the halide salt route at 800 °C for 600 s: (a) hexagonal TiB₂; (b) irregular polygon TiB₂; (c) mutual “crashing” of fragile TiB₂.

Figure 4 shows the morphology of TiAl₃ prepared by the halide salt route at 800 °C for 15 S, 30 S, or 60 S. At 800 °C for 15 S, the TiAl₃ was granular or elongated rod-shaped. When the reaction time was extended to 30 S, the strip phase became a thick rod. TiAl₃ was blocky when the reaction time was 60 S.

![Figure 4](image2)

**Figure 4.** Morphology of TiAl₃ in the Al–Ti–B Master Alloy prepared by the halide salt route after different reaction times at 800 °C: (a) 15 S; (b) 30 S; (c) 60 S.

3.2. **Morphology of TiAl₃, TiB₂ in the Ti-Sponge and Partial Ti-Sponge Route**

The reactions of preparing Al–Ti–B Master Alloy by the Ti-sponge route are shown in Formulas (4) and (5). Reaction (4) occurred spontaneously at the temperature range of 800–900 °C [19]. The mass ratio of Ti to B is 4.43:1 in reaction (4). The mass ratio of
Ti/B added to the reaction is 5:1. Therefore, reaction (5) also occurred. Figure 5 shows the X-ray diffraction pattern of the Al–Ti–B Master Alloy prepared by the Ti-sponge route with reaction times of 15 s, 300 s, and 1800 s. The diffraction peaks of the TiB₂ were observed at 15 s. AlB₂ and TiB₂ existed in the matrix simultaneously at 15 s (consistent with Formula (5)) for TiB₂ diffraction peaks broadening.

![Figure 5. XRD analysis of Al–Ti–B Master Alloy prepared by Ti-sponge route at 800 °C with different reaction times.](image)

The microstructure and EDS of Al–Ti–B Master Alloys prepared by the Ti-sponge route and partial Ti-sponge route at 800 °C for different times are shown in Figures 6 and 7. Figure 6a₁,a₂ shows different parts of the same sample. Owing to the short reaction time of 15 s, some Ti powders did not have enough time to diffuse. Therefore, the irregular white blocky TiAl₃ was observed in Figure 6a₁. Other Ti powders are relatively dispersed to form fine, rod-shaped TiAl₃ (Figure 6a₂). At a reaction time of 300 s, the whole block dispersed into small, irregular pieces (Figure 6b). The original fine, rod-shaped structure disappeared. The energy spectrum analysis indicated the white phase in Figure 6b should be pure Ti, and the surrounding gray phase should be TiAl₃. The concentration of Al in the gray phase decreased gradually from inside to outside while Ti increased. The value of Ti/Al at point 3 was closer to 36.96%, which is TiAl₃.

There are both blocky and rod-shaped TiAl₃ in Figure 8. Further, it was found that TiB₂ was embedded in blocky TiAl₃ (Figure 7b). The hexagonal holes appeared in the rod-shaped TiAl₃ and were eroded by pure Al (Figure 7a). If B was added into the Al–Ti alloy melt containing TiAl₃, then B could form TiB₂ on the TiAl₃ and cause the TiAl₃ to break or even dissolve [29]. The resulting TiB₂ will be agglomerated between the TiAl₃ and Al matrix. The reaction equation is as follows:

\[
\text{TiAl}_3(s) + 2\text{B} \rightarrow \text{TiB}_2(s) + 3\text{Al}(l)
\]  

(6)
Figure 6. The microstructure and EDS of Al–Ti–B Master Alloy prepared by the Ti-sponge route at 800 °C: (a1) 15 S reaction time—irregular blocky TiAl₃; (a2) 15 S reaction time—fine, rod-shaped TiAl₃; (b) 300 S reaction time.
3.3. Refining Effect of Al–Ti–B Master Alloy

The Al–Ti–B Master Alloy obtained at 800 °C for 1800 S using different routes was used to refine pure aluminum ingot; the refined microstructure is shown in Figure 8. The average grain sizes of pure aluminum ingot refined by halide salt route, 30% Ti-sponge route, and Ti-sponge route are 98.3 μm, 105.4 μm, and 111.8 μm, respectively. The refining effect of 30% Ti-sponge route is better than that of Ti-sponge route and worse than that of halide salt route.

The size of TiAl₃ obtained using the Ti-sponge route was larger than that using the halide salt route; they are 9.83 µm (Figure 6) and 4.7 µm (Figure 4), respectively. In the 30% Ti-sponge or 60% Ti-sponge route, the large-sized granular TiAl₃ was coexistent with the small-sized TiAl₃ (Figure 4). The size of TiB₂ particles is about 5 µm, and the size of most TiB₂ is 0.5–1.5 µm (Figure 3). The refining effect of Al–Ti–B Master Alloy is related to the size and distribution of TiAl₃ and TiB₂. A finer size and more uniform distribution of TiAl₃ and TiB₂ causes the Al–Ti–B Master Alloy to have a better grain-refining effect.
4. Discussion
4.1. Nucleation and Growth of TiAl₃ and TiB₂ in Different Ti Adding Routes—The Ti–TiAlₓ Mechanism

The nucleation of TiAl₃ mainly depends on the mutual diffusion of Al and Ti for the Ti-sponge route. This diffusion process makes TiAlₓ form around the pure Ti particles first, as shown in Figure 6b. As diffusion progresses, the external TiAlₓ is separated into single TiAl₃, but the concentration of internal Ti remains high (Figure 6a). Finally, the TiAlₓ completely converted into separated TiAl₃ after 300 S reaction at 800 °C (Figure 6b). This mechanism is called the Ti–TiAlₓ mechanism for the Ti-sponge route, as shown in Figure 9.

Sunda [30] proposed that Ti–Al’s interdiffusion coefficient (D) is a function of composition and temperature; D increases with increasing temperature when the composition is constant. The diffusion activation energy of aluminum (Q) is different in different phases, but Q is substantially constant and independent of the concentration. We have the following order: Q[TiAl₃] > Q[TiAl] > Q[α-Ti(Al)] > Q[β-Ti(Al)]. Obviously, the diffusion coefficient of Al in Ti₃Al is smaller than that in Ti particles. Therefore, Al enriched on the Ti particle’s surface passed through the TiAl₃ layer (Figure 9) resulting in a high concentration of Al surrounding the surface of the Ti particles. Thus, TiAlₓ is constantly formed and eventually converted into separate TiAl₃.

The nucleation mechanism of the rod-shaped TiAl₃ (Figure 6a₂) is different from the Ti–TiAlₓ mechanism. The atomic ratio of Ti to KBF₄ is 1:1 in reaction (4). Actually, the ratio of Ti to KBF₄ is about 1.13:1 in this experiment so that KBF₄ can react completely. The rod-shaped TiAl₃ comes from reaction (4) and is easy to dissolve versus blocky TiAl₃; therefore, it almost disappeared after 300 S of reaction (4), as shown in Figure 6b. For the Ti-sponge route, Ti is involved in the transition of Ti–TiAlₓ to produce TiAl₃, which leads to the deficiency of Ti and excess of B. The B can form TiB₂ on the TiAlₓ and cause TiAl₃ to break and be dissolved. The long, rod-shaped TiAl₃ is more easily dissolved than the block-shaped TiAl₃ [31]. Therefore, in the Ti-sponge route, the initial formation of the rod-shaped TiAl₃ does not stay easily in the melt, which is different from the characteristic of the halide salt route. However, there is still a rod-shaped TiAl₃ in the microstructure of the Al–Ti–B Master Alloy prepared by the 30% Ti-sponge route with the reaction temperature of 800 °C for 900 S. The total amount of Ti is constant, and with less free Ti content, there is less of a Ti–TiAlₓ mechanism. When there is less excess B, some of the rod-shaped TiAl₃ are retained and less Ti is consumed in the melt.

Section 3.1 shows that the “rich Ti, B area” is the birthplace of the nucleation and growth of initial TiAl₃ and TiB₂ for the halide salt route. Similarly, the “rich Ti, B area” are also found in the partial Ti-sponge route as shown in Figure 10b. The “rich Ti, B area”
gradually decreased with increasing Ti powder content; only a small amount of filamentous and small strip regions were formed in the Ti-sponge route. In Ti-sponge route, a lot of Ti powder is directly involved in the formation of TiAl₃ by the Ti–TiAlₓ mechanism. During the nucleation and growth of TiAl₃, the blocky Ti powder seriously hindered the diffusion of Ti into the Al melt, thus resulting in insufficient Ti in the melt. The insufficient diffusion of Ti also severely reduced the amount of Ti involved in the reaction (4), thus reducing the “rich Ti, B area” in the melt.

**Figure 10.** The “rich Ti, B area” in different Al–Ti–B Master Alloy prepared routes at 800 °C for 15 S: (a) halide salt route; (b) 60% Ti-sponge route; (c) Ti-sponge route.

The Ti addition routes have greatly influenced the morphology and size of TiAl₃. The size of TiAl₃ formed based on the Ti–TiAlₓ mechanism in the Ti-sponge route is coarse. Ti and Al diffused mutually in the TiAlₓ around the Ti particles, and the outer TiAl₃ is mainly separated into small blocks. The “rich Ti, B area” in the Ti-sponge route under the influence of the Ti–TiAlₓ mechanism is a small amount that cannot meet the TiB₂ growth well. Due to the Ti–TiAlₓ mechanism, the diffusion efficiency of Ti in Ti-sponge route is much lower than halide salt route. TiAlₓ formed based on the chemical reaction (4) is long and rod-shaped. The long, rod-shaped TiAl₃ cannot exist stably in the melt due to the excess B and lack of Ti in the pre-reaction melt. Therefore, it does not appear in the final microstructure.

### 4.2. Evolution Mechanism of TiB₂ with Irregular Polygon

In addition to reaction (1), the following reaction may produce TiB₂ when the Al–Ti–B Master Alloy is prepared by the halide salt route [32]:

\[
\text{AlB}_2(s) + \text{Ti} \rightarrow \text{TiB}_2(s) + \text{Al}(l) \tag{7}
\]

\[
2\text{B} + \text{Ti} \rightarrow \text{TiB}_2(s) \tag{8}
\]

Here, TiB₂ is nucleated by the fluorination reaction and grown in the rich Ti and B area based on the above two reactions. Figure 11 shows the microstructure of the TiB₂ when the mixed fluoride salt is added into the aluminum melt at 800 °C for 10 S–600 S using the halide salt route.

The TiB₂ was an irregular small particle at the initial stage of the reaction (10 S and 15 S). Regular hexagonal TiB₂ particles appeared with longer reaction times to 20 S and 30 S, and the size of TiB₂ was about 0.5 μm. At 60 S, the size of TiB₂ particle continued to increase. At 5 min, some TiB₂ collided together and cracks appeared along the junction of particles. At a reaction time of 10 min, the size of TiB₂ particles reached 1.5 μm and there were a lot of lug boss' around the TiB₂ particles. According to the reaction (7), the filamentous AlB₂ (corresponding to (Tiₓ, Al₁₋ₓ)₂B₃ in Figure 1a) was more likely to be destroyed when it was transformed into TiB₂ [33]. Therefore, TiB₂ was more easily crushed with increasing reaction time.
The crushing of TiB₂ is related to the crystal structure. Figure 12a,c represent the crystal growth model of TiB₂ [34]. TiB₂ belongs to hexagonal system (the lattice parameters $a = 0.3030$ nm, $c = 0.3232$ nm, $c/a = 1.0818$). The growth direction extends longitudinally in the direction of $<0001>$ or extends laterally in the direction of $<1\bar{1}00>$. The growth rate is the slowest because the {0001} surface has the highest atomic density and the lowest surface energy. Thus, the longitudinal growth rate of TiB₂ is lower than the lateral expansion speed. The lug boss in $<0001>$ direction and the projecting lug in $<1\bar{1}00>$ direction were also observed, as shown in Figure 12b,d,e.

Figure 11. Morphology of TiB₂ for the halide salt route at 800 °C for different reaction times.

Figure 12. Schematic diagram and microstructure of possible defects in the earlier and later growth stage of TiB₂ for the Al–Ti–B Master Alloy prepared by the halide salt route: (a) earlier TiB₂ crystal growth model; (b) earlier actual growth of TiB₂; (c) later TiB₂ crystal growth model; (d,e) later actual growth of TiB₂.
In the nucleation of TiB$_2$, the generation and expansion mechanism of lug boss plays a significant role. The contents of Ti and B in the “rich Ti, B area” are sufficient, and the TiB$_2$ (0001) surface is small and provides favorable conditions for the formation of lug boss. When the lug boss is generated in the [1] direction, the lug boss rapidly expands the entire (0001) plane, and the thickness and size of the TiB$_2$ quickly increase. The nucleation of TiB$_2$ is similar to the layered stacking pattern according to the above mechanism (Figure 12a,b). There may be parallel surface defects between the new layer formed by the lug boss and the original layer. The formation and expansion mechanism of the projecting lug play a significant role during the TiB$_2$ growth. The Ti and B in the “rich Ti, B area” were partially consumed at TiB$_2$ growth stage. The growth of the [0001] plane requires larger surface energy, which makes the formation and expansion of the lug boss difficult. Therefore, the thickness of the TiB$_2$ does not change. The growth of TiB$_2$ is the lug generation and expansion in the direction $<1\overline{1}00>$.

Figure 12c–e show that many lugs in the [1100] plane are prone to producing crystal defects during simultaneous growth. When the two lugs grow in parallel, there may be a planar defect parallel to the [1100] plane between the upper and lower lugs. When the two lugs grow side by side, between the left and right lugs, it is possible to form a planar defect perpendicular to the [1100] plane. The [1100] plane is not flat when the lug stops the growth eventually due to the lack of Ti and B.

The crushing of the TiB$_2$ is also related to the growth environment. Figure 13 shows the microstructure of the “rich Ti, B area” for the halide salt route at 800 °C for 60 S. The TiB$_2$ was rich in “rich Ti, B area” and many TiB$_2$ particles were clustered together during the growth process. This aggregation phenomenon can also crush TiB$_2$. It is difficult to ensure uniform growth in all directions; thus, TiB$_2$ has an irregular morphology.

![Figure 13. SEM of the “rich Ti, B area” and TiB$_2$ in the Al–Ti–B Master Alloy prepared by the halide salt route at 800 °C for 60 S.](image)

5. Conclusions

(1) The fluorine salt reaction occurred very fast when Al–Ti–B was prepared by the halide salt route (<10 S). A streamlined “rich Ti, B area” exists in the aluminum melt in the initial stage of the reaction ((800 °C, <30 S). This is a complex compound of (Ti$_x$, Al$_{1-x}$)$_y$. The “rich Ti, B area” is essential for the nucleation and growth of TiAl$_3$ and TiB$_2$.

(2) The Ti addition route greatly influences the morphology of TiAl$_3$. The formation of TiAl$_3$ using the Ti-sponge route is based on the Ti–TiAl$_x$ mechanism. The nucleation of TiAl$_3$ mainly depends on the mutual diffusion of Al and Ti powder, and TiAl$_x$ formed around the Ti particles. The TiAl$_3$ formed based on the Ti–TiAl$_x$ mechanism is mainly block-shaped and the average size is 9.83 μm. In the halide salt route, TiAl$_3$ formation is based on the reaction of Ti powder and KBF$_4$ to form a rod-shaped TiAl$_3$. The long, rod-shaped TiAl$_3$ disappeared due to excess B and a lack of Ti in the aluminum melt. Finally, small blocks of TiAl$_3$ formed with an average size of 4.7 μm.
(3) TiB$_2$ particles showed different morphologies at different reaction times when the Master Alloy was prepared by the halide salt route. The TiB$_2$ was an irregular and small particle at the initial stage of the reaction (10 S and 15 S). Regular hexagonal TiB$_2$ particles appeared as the reaction time increased to 20 S and 30 S. The size of TiB$_2$ was about 0.5 µm. The size of TiB$_2$ particle continued to increase at 60 S. Some TiB$_2$ collided together at 5 min. Both the crystal defects and the crowded growth environment caused by the “rich Ti, B area” are the fundamental reasons for the fragility and irregular shape of the TiB$_2$.

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