

Article

Refinement Properties and Refinement Mechanism of a New Master Alloy Al-5Ti-1B-1RE Refiner

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Abstract: To obtain high-quality grain refiner, a new Al-5Ti-1B-1RE master alloy grain refiner was synthesized by the melt-matching method. Its microstructure and refining effect, refining properties, and refining mechanism were analyzed. The experimental results show that the second-phase particles of Al-5Ti-1B-1RE master alloy are mainly TiB₂, Al₃Ti, Ti₂Al₂₀RE, etc. The magnitude of the free energy ΔG of the synthesis reaction is calculated to be $\Delta G_{\text{TiB}_2} < \Delta G_{\text{Al}_3\text{Ti}} < \Delta G_{\text{Ti}_2\text{Al}_{20}\text{RE}}$. The nucleation rate N mainly depends on the kinetic atomic diffusion activation energy Q and the thermodynamic nucleation work. The microstructure of commercial pure aluminum refined by the new grain refiner has almost transformed from coarse columnar crystals to fine equiaxed crystals, with an average grain size of 70.2 μm , which was 36.18% and 20.66% smaller than that refined by domestic and imported Al-Ti-B wire master alloy grain refiner, its mechanical properties of tensile strength σ_b were increased by 11.94% and 8.29%, and elongation δ was improved by 31.79% and 17.41%, respectively. The main refinement mechanism is the formation of TiAl₃ on TiB₂ particles and the release of RE atoms from the Ti₂Al₂₀RE phase, which in turn is partially transformed into the TiAl₃ phase, which promotes dual nucleation refinement.

Keywords: Al-5Ti-1B-1RE master alloy; commercial pure aluminum; refinement effect; refine performance; double nucleus refinement mechanism



Citation: Wang, Z.; Wang, S.; Yang, Q.; Liu, X.; Dong, C.; Liu, L. Refinement Properties and Refinement Mechanism of a New Master Alloy Al-5Ti-1B-1RE Refiner. *Coatings* **2024**, *14*, 1485. <https://doi.org/10.3390/coatings14121485>

Academic Editor: Elena Villa

Received: 26 October 2024

Revised: 20 November 2024

Accepted: 22 November 2024

Published: 25 November 2024



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1. Introduction

Aluminum and aluminum alloys have a wide range of applications in aerospace, manufacturing, transportation, and mobile communications in automotive and other fields due to their excellent thermal conductivity, low density, high specific strength, and good process properties [1–3]. The grain refinement treatment of aluminum and aluminum alloys has always been a research hot spot. Since the introduction of the Al-Ti-B master alloy grain refiner, it has rapidly become the most efficient and widely used grain refiner in aluminum and aluminum alloys with a high-efficiency grain refining effect, which is a major breakthrough in grain refining treatment technology [4]. It is currently used by approximately 75% of users worldwide and is recognized as one of the most effective grain refiners for aluminum and aluminum alloys [5]. With the increasing application of Al-Ti-B master alloy grain refiners in the modern aluminum industry, it has been found that their performance defects limit their use in the rolling of high-grade foil materials. The refining effect of high-strength aluminum alloys containing elements such as Zr and Cr is weakened or even lost, resulting in uneven grain structure, known as the “grain refiner poisoning” phenomenon, making it difficult to obtain high-quality aluminum products [6,7]. And with the increasing use of aluminum and aluminum alloys, the demand for high-quality grain refiners is also increasing. Due to the late start of research on grain refiners in China and the blockade of related core technologies by foreign countries, the second particles TiAl₃ and TiB₂ in the prepared Al-Ti-B grain refiners have larger sizes, fewer quantities,

and more severe agglomeration. The refinement effect and product purity are significantly inferior to similar foreign products, and high-quality Al-Ti-B grain refiners need to be imported in large quantities [8]. Therefore, the development of an efficient, clean, and stable grain refiner is imminent to solve the shortage of the Al-Ti-B grain refiner, which is of great practical significance and economic benefits to the development of China's aluminum processing industry.

Therefore, domestic and foreign materials science and technology workers have been exploring a new generation of grain refiner, which will reduce or eliminate "grain refiner poisoning", as a key topic of current research. In recent years, it has been found that the role of rare earth refinement, purification, and other functions and the refinement of Al-5Ti-1B master alloy can be effectively combined to develop a new type of Al-5Ti-1B-1RE master alloy grain refiner, which can significantly improve the refining performance of the grain refiner and can reduce or eliminate the phenomenon of "grain refiner poisoning" [9,10]. The synthesis and preparation methods of the Al-5Ti-1B-1RE master alloy are constantly evolving and improving, with various advantages and disadvantages for each synthesis method [11–14]. However, the melt-matching method has the advantages of fast reaction, low synthesis temperature, low energy consumption, and low pollution and stands out among many synthesis methods [15–17]. A new Al-5Ti-1B-1RE master alloy grain refiner was synthesized by introducing rare earth elements during the synthesis of Al-Ti-B master alloy. A large amount of research has been conducted to improve the grain refinement performance of the Al-5Ti-1B-1RE grain refiner, and certain achievements have been made, but substantial breakthroughs have not yet been achieved. The reasons for this are related to the lack of systematic and detailed thermodynamics calculations and kinetic analysis of the preparation process of the Al-5Ti-1B-1RE grain refiner, the lack of in-depth research on the refining mechanism and the control of the second phase, and the lack of key technologies. This is the bottleneck in the development of obtaining a high-quality Al-5Ti-1B-1RE grain refiner. At present, the research on the grain refinement mechanism of aluminum and aluminum alloys mainly focuses on two aspects [18,19]: first, the theoretical research on the modeling method of the grain refinement mechanism of aluminum and aluminum alloys. Second, based on the theoretical study, the refinement methods of aluminum and aluminum alloys are formulated and optimized, which mainly include physical methods such as controlling the cooling rate, vibration, stirring, and ultrasonic treatment of the melt, and chemical methods such as the addition of grain refiners. At present, there are various nucleation theories in the study of the refinement mechanism of the Al-5Ti-1B-1RE grain refiner, but no consensus has been reached [20–22]. The fine dispersed second phase in the grain refiner is the key for improving their refining performance and has been recognized. In this paper, thermodynamic calculations, kinetic analysis, and the refinement mechanism of Al-5Ti-1B-1RE grain refiner synthesis and preparation were carried out in order to provide a useful reference for the research and development of high-quality grain refiners. It also provides a solid theoretical foundation and practical reference value for fully tapping into the potential of materials, expanding the application of aluminum and aluminum alloys in China's new energy vehicles and meeting the demand for lightweight manufacturing.

2. Materials and Methods

2.1. Test Materials

The main materials used are commercial pure aluminum ($w(\text{Al})\% \geq 99.70\%$), aluminum powder, potassium fluoroborate ($w(\text{KBF}_4) \geq 98.00\%$), titanium powder ($w(\text{Ti})\% \geq 99.00\%$), cerium lanthanum-rich rare earth, as shown in Table 1, hexachloroethane (C_2Cl_6), covering agent, grain refiner, degassing agent, coating, graphite stirring rod, JJ-1 precision booster electric mixer, and other auxiliary materials and tools. When calculating the alloy element composition, the upper limit value of the burning loss is taken for the alloy elements with high burning loss.

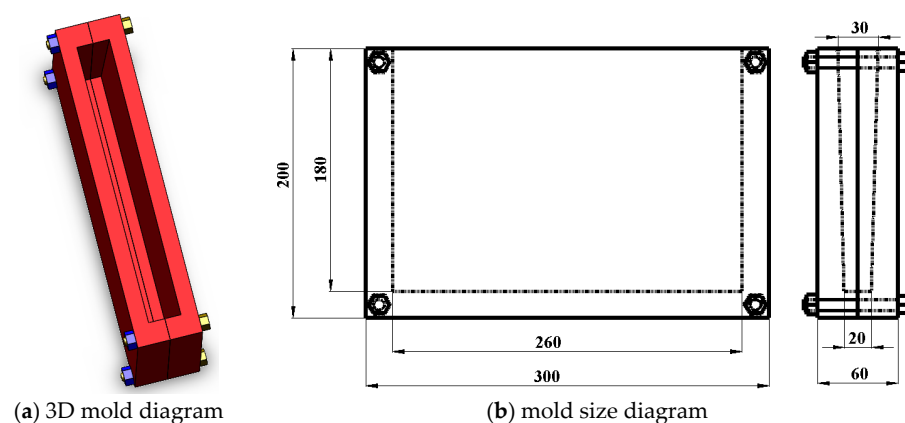
Table 1. The chemical compositions of cerium lanthanum-rich rare earth (wt.%) [23].

Ce	La	Nd	Pr	Sm	Fe	Mg	Si	Zn	C
53~57	20~24	14~18	3~7	0.3	0.5	0.1	0.03	0.07	0.06

2.2. Methods

2.2.1. Al-5Ti-1B-1RE Master Alloy Synthesized by Melt-Matching Method

After the titanium powder, aluminum powder, potassium fluoroborate (KBF_4), and hexachloroethane (C_2Cl_6), which were removed from the water, were proportioned according to the appropriate stoichiometric ratios, they were fully ball-milled on a high-speed ball mill then taken out and pressed into blocks under a certain amount of stress on a universal test tensile machine. Then, the graphite crucible containing a certain quality of pure aluminum was placed in the SG2-7.5-12 well type resistance furnace produced by Xinyu New Material Technology Co., Ltd. in Nanyang City, China, and was heated up to $730\text{ }^\circ\text{C}$. A certain thickness of special covering agent was added on the surface of Al melt, and it was stirred and stripped of slag after the pure aluminum was completely melted. The furnace temperature was raised to $830\text{ }^\circ\text{C}$, the treated briquettes and mixed rare earth RE were wrapped with aluminum foil and then pressed into the middle and lower part of the melt in batches with graphite bellows, the aluminum melt was stirred with graphite rods and a JJ-1 precision power increasing electric stirrer, and the reaction was fully carried out by holding the temperature for 20 min and stirring once every 5 min to fully react. The temperature was lowered to $780\text{ }^\circ\text{C}$ and the alloy liquid was refined and degassed and stood for 5 min until the slag floated up. The slag was thoroughly removed, and the alloy liquid in the crucible was poured into the mold and cooled to room temperature in air to synthesize the Al-5Ti-1B-1RE master alloy grain refiner. The casting mold is shown in Figure 1. The phase analysis of the Al-5Ti-1B-1RE master alloy was carried out using a high-power (18 KW), high-precision, and fast positioning D/Max-2500/pc X-ray diffractometer from Nippon Rikyu, Kyoto, Japan. The test parameters are as follows: scanning type: continuous scanning, scanning mode: 2 Theta/Theta, $\text{CuK}_\alpha = 0.154056\text{ nm}$, $\text{KV} = 40\text{ kV}$, $\text{mA} = 200\text{ mA}$, sampling $W = 0.02$, scan speed = $6.000^\circ/\text{min}$, start angle = 15.000° , Stop angle = 90.000° . The chemical composition analysis was carried out using a German Spike SPECTRO MAXx mm06 direct reading spectrometer from Spike, Kleve, Germany. The microstructure of the second phase was analyzed using a Hitachi S-3400N scanning electron microscope (SEM) with an acceleration voltage of 0.3 kV – 30 kV , energy dispersive X-ray spectroscopy (EDX) from Hitachi, Tokyo, Japan and a JEM-2100 high-resolution transmission electron microscope (TEM) from Japan Electronics Corporation, Tokyo, Japan with an acceleration voltage of 200 kV . The refinement effect of commercial pure aluminum was observed and analyzed using a LEICA DM 2500M optical microscope (OM) from Solms, Germany. The grain sizes were measured by the professional particle size analysis software “Nano Measurer 1.2”.

**Figure 1.** Casting mold.

2.2.2. Refinement Test Process

The graphite crucibles containing equal mass of pure aluminum were placed in four well resistance furnaces of KSL-12-JY type with the same conditions to be heated, and the temperature was raised to 730 °C. After the aluminum melts were completely melted, slag removal, degassing, refining, and slag removal were performed, and the pure aluminum was poured into the first graphite crucible. Then, the domestic, imported Al-5Ti-1B wire master alloy refiner and homemade Al-5Ti-1B-1RE master alloy refiners were added to the molten pure aluminum in each of the other three graphite crucibles. The actual production of the amount of addition as a standard is 0.20% of the aluminum melt, that is, Ti (wt.%) = 0.01%. The aluminum melts were thoroughly stirred and held for 5 min. After slag removal, degassing, refining, and slag removal, these three aluminum melts were poured in sequence.

2.2.3. The Metallographic Analysis and Mechanical Test

After cooling, the poured specimens were prepared into metallographic and tensile specimens. The cross-sections of the specimens were taken from the center of the cast specimens. Longitudinally, the specimens were taken from the center of 1/2 of the bottom surface. The size of the metallographic specimens was 10 mm × 10 mm × 15 mm rectangular. The tensile test specimens were processed according to the standard GB/T16865-2013 [24] and subjected to tensile performance testing on the WDW-10 microcomputer-controlled electronic universal testing machine. The total length of the tensile specimens was 190 mm, of which the length of the two clamped ends of the specimen was 50 mm, the diameter of the original cross-section of the parallel length of the specimen was 12.5 mm, and the specimen marking distance before the application of force at room temperature was 70 mm, as shown in Figure 2. The tensile speed was 0.5 mm/min at room temperature. After pulling off the two parts of the specimen closely butted together, the axis of the two parts was located in the same straight line, measuring the specimen after pulling off the standard distance. The tensile strength σ_b is the stress corresponding to the maximum test force N_b of the specimen during pull-off, and its value was the maximum test force divided by the original cross-sectional area A_0 of the specimen [25]:

$$\sigma_b = \frac{N_b}{A_0} \quad (1)$$

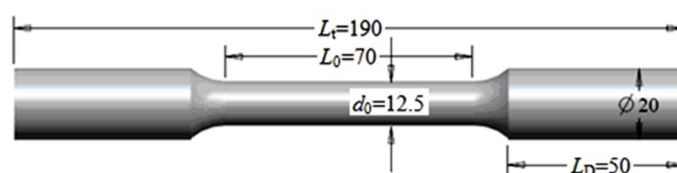


Figure 2. Geometry of tensile specimen at room temperature (mm).

The elongation after fracture δ was the percentage of the elongation of the gauge length of the specimen after fracture to the original gauge length

$$\delta = \frac{L_1 - L_0}{L_0} \times 100\% \quad (2)$$

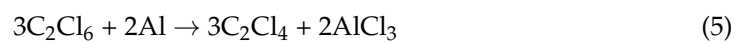
where L_0 —the original gauge length of the specimen; L_1 —the gauge length of the sample after being pulled apart.

To ensure the accuracy of the tensile test data, 5 specimens were stretched in each group, and the average value was taken.

3. Results

3.1. Phase Analysis of Grain Refiner for Al-5Ti-1B-1RE Master Alloy

In the process of synthesis and preparation of the Al-5Ti-1B-1RE master alloy, when hexachloroethane was pre-pressed into blocks and pressed into the aluminum liquid, the absorption rate of the reactants can be greatly increased. The main reason for this was that hexachloroethane produced a large amount of gas at high temperatures, which can play a role in rapid stirring, so that the aluminum powder, titanium powder, and potassium fluoroborate were fully dispersed and in contact with the melt. C_2Cl_6 is a white crystal with a density of 2.091 g/cm^3 and a sublimation temperature of 185.5°C . It produces the following reaction when pressed into an aluminum liquid [26]:



The boiling point of the reaction product C_2Cl_4 is 121°C , and it participates in refining together with $AlCl_3$ so that the titanium powder and potassium fluoroborate absorption can be greatly improved. The Al-5Ti-1B-1RE master alloy grain refiner synthesized at a reaction temperature of 830°C was subjected to X-ray diffraction phase analysis, as shown in Figure 3.

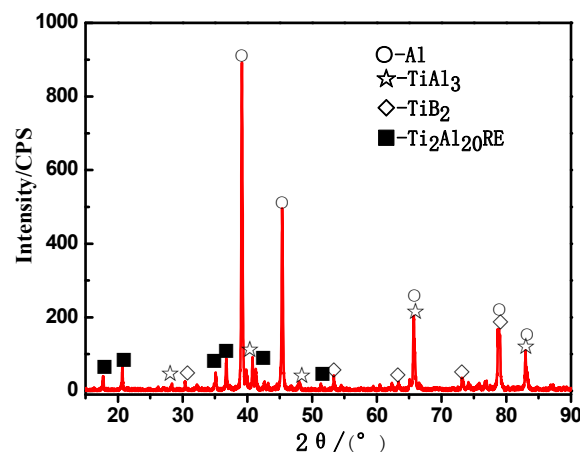
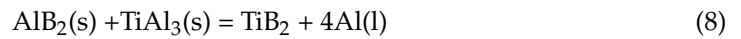


Figure 3. X-ray diffraction pattern of Al-5Ti-1B-1RE master alloy refiner.

From Figure 3, it can be seen that during the reaction process, in addition to the diffraction peaks of Al phase, there are also diffraction peaks of $TiAl_3$, TiB_2 , and $Ti_2Al_{20}RE$ phases. This indicated that Ti, which was supersaturated in the Al melt, should have been synthesized with Al to form the $TiAl_3$ phase. However, due to the introduction of RE elements, its activity in the Al melt was very high and the surface energy was also very high in order to reduce the surface energy, and its solid solubility in the aluminum melt was very low, so there was a free state of the RE elements involved in the reaction of Al and Ti to generate the $Ti_2Al_{20}RE$ phase, i.e., $Ti_2Al_{20}Ce$ and $Ti_2Al_{20}La$ phase. Due to the fact that KBF_4 and Ti powder were added to the aluminum melt in the form of pressed blocks, the atomic density and reactivity were significantly lower than those of RE added in bulk. Therefore, they preferentially interacted with the Al melt. It mainly underwent the following reactions (6)–(9) [27]:





As the synthesis reaction proceeded the $\text{Ti}_2\text{Al}_{20}\text{RE}$ phase was increasing and the amount of TiAl_3 phase was decreasing. However, the reaction (7) proceeded sufficiently due to the excess of added Ti elements, so there was still residual TiAl_3 phase present in the Al melt after TiAl_3 was fully involved in the reaction (9). The TiB_2 phase was very stable, and it did not react with RE, and no titanium–boron rare-earth compounds were detected at the end of the reaction. So, the second phase in the synthesized and prepared refiner was mainly TiAl_3 , TiB_2 , and $\text{Ti}_2\text{Al}_{20}\text{RE}$ phases, as shown in Figure 3. The chemical composition of the synthesized and prepared Al-5Ti-1B-1RE master alloy refiner was examined, as shown in Table 2, and from the data, it can be indicated that the synthesized chemical composition achieved the chemical composition of the design goal.

Table 2. The chemical compositions of Al-5Ti-1B-1RE master alloy (wt.%).

Alloying Element	Ti	B	RE	Fe	Si	Cu	Ni	Al
Nominal composition	5.00	1.00	1.00	≤0.20	≤0.20	≤0.10	≤0.10	Bal
Actual measurement value	5.06	0.93	0.95	0.14	0.12	0.04	0.05	Bal

The synthesis reaction temperature was 830 °C, and the microstructure of the SEM is shown in Figure 4, in which the size of the larger gray block, with obvious angular phase, is pointed out in Figure 4a. After further analysis by energy dispersive X-ray spectroscopy, as shown in Figure 4b, it mainly contained two elements of aluminum and titanium, with an atomic percentage content ratio of $\text{Ti}:\text{Al} \approx 1:3$, which can be determined as TiAl_3 . The appearance shape was similar to TiAl_3 , with a larger size and a whitish surface, as indicated by B in Figure 4. According to the energy spectrum analysis, as shown in Figure 4c, it mainly contained titanium, aluminum, and rare-earth elements, with an atomic percentage ratio of $\text{Ti}:\text{Al}:\text{RE} \approx 2:20:1$. Based on Figure 3, it can be determined that the $\text{Ti}_2\text{Al}_{20}\text{RE}$ phase was composed of Al, Al_3Ti , and RE and had a complex face-centered cubic structure. The small-sized black-gray particles distributed in the matrix, as indicated by C in Figure 4, were analyzed by energy spectrum. As shown in Figure 4d, they mainly contained two elements, titanium and boron, and were distributed in the aluminum matrix. Their atomic percentage ratio was $\text{Ti}:\text{B} \approx 1:2$. Combined with Figure 3, it can be determined that they were TiB_2 phase, which had good chemical stability and did not react with RE. RE mainly acted as a surfactant, dispersant, and catalyst in aluminum melt, adsorbing and forming a liquid film at the solid–liquid interface, hindering the contact between particles, reducing the surface tension of the interface, reducing the contact and repulsive force between second phase particles, reducing agglomeration, and making TiB_2 particles more evenly distributed. It was extremely beneficial for improving the surface wettability and grain refinement of TiAl_3 and TiB_2 in aluminum melt.

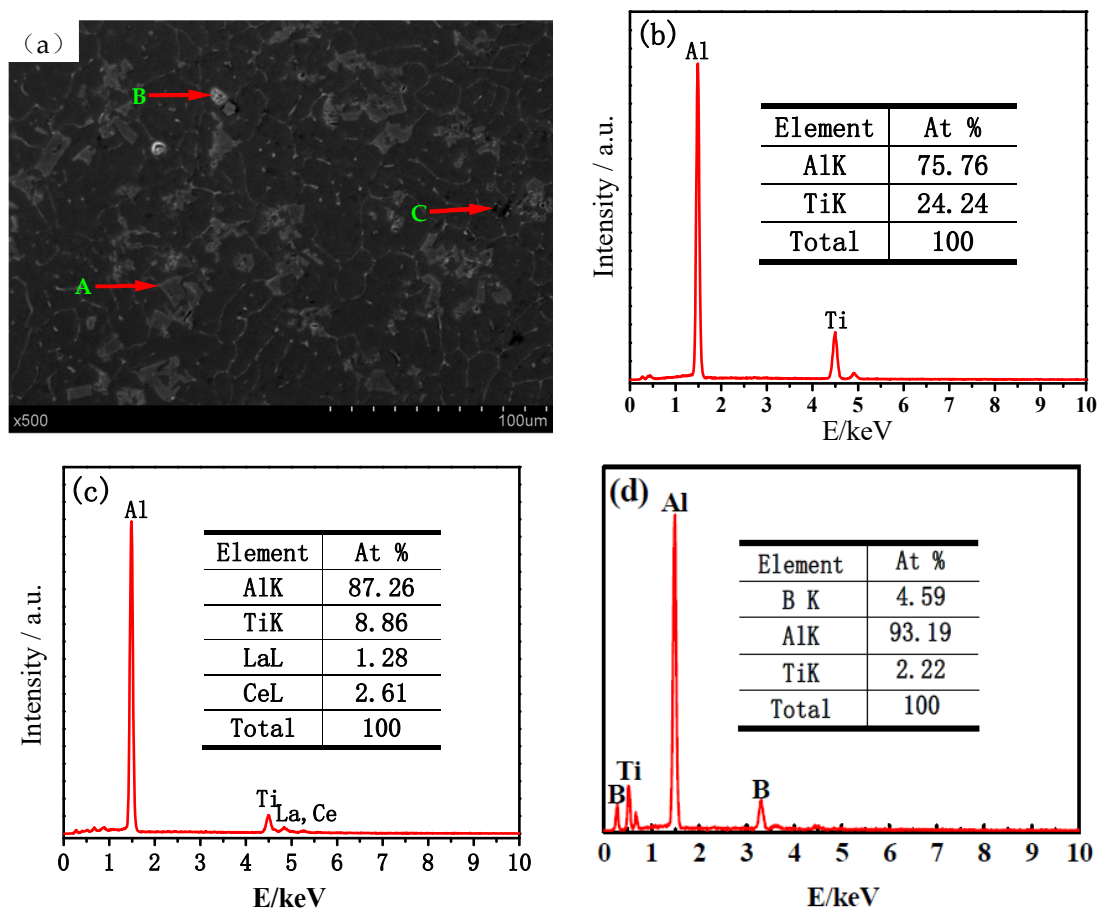


Figure 4. The microstructures of the second phase particles: (a) and EDAX of the secondary phases of Al-5Ti-1B-1RE master alloy: (b) A phase; (c) B phase; (d) C phase.

From the TEM image of TiB_2 in the Al-5Ti-1B-1RE master alloy at a synthesis temperature of 830 °C in Figure 5, it can be clearly observed that TiB_2 had a relatively regular hexagonal shape with a tendency to aggregate, as indicated by the red arrow in Figure 5. TiB_2 particles aggregated together, with a cluster size of approximately 1.2 μm, while the size of the individual TiB_2 particles is about 0.6 μm, as indicated by the arrows in Figure 5. When evaluating TiB_2 contained in aluminum master alloy refiners, the standard specifies [28] the size of loose TiB_2 agglomerates ≤ 25 μm, the presence of no dense TiB_2 agglomerates, and TiB_2 particles with a size ≤ 2 μm should account for more than 90% with a roughly uniform and dispersed distribution. The TiB_2 agglomerate size in the Al-5Ti-1B-1RE master alloy prepared at synthesis temperature was approximately $1.0 \mu\text{m} \leq 25 \mu\text{m}$, with more than 90% of TiB_2 particles having sizes $\leq 2 \mu\text{m}$ and no dense TiB_2 agglomerates present. This indicated that the TiB_2 particle size in the grain refiner prepared by this process had reached the standard specification.

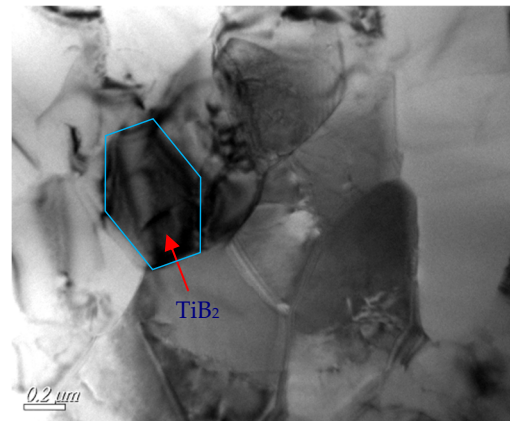


Figure 5. TEM of TiB_2 of Al-5Ti-1B-1RE master alloy at synthetic temperature 830 °C.

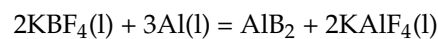
3.2. Calculation and Analysis of Thermodynamics

Computational analysis of thermodynamics, which was seriously missing from the study of key issues in the preparation process, was carried out during the synthesis of Al-5Ti-1B-1RE master alloys prepared by the melt-matching method due to the approximate Ti/B mass ratio of 5:1, exceeding the mass ratio of Ti and B in TiB_2 (2.2:1). Therefore, the main reaction products of KBF_4 and Ti in the aluminum alloy melt at atmospheric pressure 1103.15 K (temperature 830 °C) are AlB_2 , TiAl_3 , and TiB_2 , whose thermodynamic calculations were in accordance with the conditions of the standard reaction heat effect method calculations, which were carried out by the Kirchhoff equations for the first approximation of the standard reaction heat effect [29]:

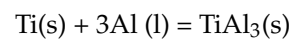
$$\Delta G_T^\theta = (\Delta H_{298}^\theta \pm \Sigma \Delta H_{\text{phase}}) - T(\Delta S_{298}^\theta \pm \Sigma \frac{\Delta H_{\text{phase}}}{T_{\text{phase}}}) \quad (10)$$

where: ΔH_{phase} and $\frac{\Delta H_{\text{phase}}}{T_{\text{phase}}}$ are the heat and entropy of phase transition of a substance. If the substance undergoing phase transition is a product in the reaction, it is marked with a positive sign, and if it is a reactant, it is marked with a negative sign.

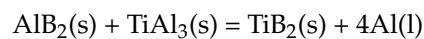
During the synthesis of the prepared Al-5Ti-1B-1RE master alloys by the melt-matching method, the main reactions occurring were as follows:



$$\begin{aligned} \Delta G_1^\theta(\text{AlB}_2) &= -48,072 + 36.363T \\ &= -48,072 + 36.363 \times 1103.15 = -7928.15655 \end{aligned} \quad (11)$$



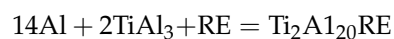
$$\begin{aligned} \Delta G_2^\theta(\text{TiAl}_3) &= -18,227 + 15.712T \\ &= -18,227 + 15.712 \times 1103.15 = -894.3072 \end{aligned} \quad (12)$$



$$\begin{aligned} \Delta G_3^\theta(\text{TiB}_2) &= -73,381 + 38.996T \\ &= -73,381 + 38.996 \times 1103.15 = -30,362.5626 \end{aligned} \quad (13)$$

According to the thermodynamic data for the standard reaction Gibbs free energy change $\Delta G \leq 0$, the reaction proceeds spontaneously to the right. When the synthesis temperature was 1103.15 K (830 °C), it was calculated that (1) $\Delta G_1^\theta(\text{AlB}_2) = -48,072 + 36.363 \times 1103.15 = -7928.15655 \text{ kJ} \cdot \text{mol}^{-1} < 0$, AlB_2 can be produced in the aluminum melt. When $\Delta G_1^\theta(\text{AlB}_2) \geq 0$, the temperature $T_1 \geq 1322.00 \text{ K}$ (1048.85 °C), the reaction (11) proceeded to the left and

AlB_2 cannot stabilize, since the refiner synthesis temperature was at atmospheric pressure $830\text{ }^\circ\text{C} < 1048.85\text{ }^\circ\text{C}$, AlB_2 can stabilize at $830\text{ }^\circ\text{C}$. (2) $\Delta G_2^\theta(\text{TiAl}_3) = -18,227 + 15.712 \times 1103.15 = -894.3072\text{ kJ}\cdot\text{mol}^{-1} < 0$, reaction (12) proceeded to the right to generate TiAl_3 . When $\Delta G_2^\theta(\text{TiAl}_3) \geq 0$, the temperature $T_2 \geq 1160.07\text{ K}$ ($886.92\text{ }^\circ\text{C}$), reaction (12) proceeded to the left, and TiAl_3 could not exist stably. TiAl_3 decomposed and dissolved. Since the synthesis temperature of the grain refiner was at atmospheric pressure $830\text{ }^\circ\text{C} < 886.92\text{ }^\circ\text{C}$, TiAl_3 could exist stably at $830\text{ }^\circ\text{C}$. (3) $\Delta G_3^\theta(\text{TiB}_2) = -73,381 + 38.996T_3 = -73,381 + 38.996 \times 1103.15 = -30,362.5626\text{ kJ}\cdot\text{mol}^{-1} < 0$, reaction (13) proceeded to the right, producing TiB_2 , which had a much lower free energy ΔG than AlB_2 . When $\Delta G_3^\theta(\text{TiB}_2) \geq 0$, $T_3 \geq 1881.76\text{ K}$ ($1608.61\text{ }^\circ\text{C}$), the reaction (13) proceeded to the left and TiB_2 cannot be stabilized. TiB_2 can be stabilized in the synthesis process at atmospheric pressure of $830\text{ }^\circ\text{C}$. After adding Al-5Ti-1B-RE refiner to the melt, Al_3Ti was dissolved, and excess Ti was released into the melt. Due to the more negative Gibbs free energy of TiB_2 compared to AlB_2 and Al_3Ti , from a thermodynamic perspective, AlB_2 was extremely unstable in high-temperature Al-Ti-B-RE melts. As the reaction time prolonged, the transformation of AlB_2 to TiB_2 occurred. At the same time, the melting point of AlB_2 ($950\text{ }^\circ\text{C}$) was much lower than that of TiB_2 phase ($2980\text{ }^\circ\text{C}$), so Ti in the melt tends to combine with B to form TiB_2 . According to the principle of minimum energy in the system, the system always needs to adjust itself to reach the lowest energy and be in a stable equilibrium state. Therefore, reaction Equation (8) was sufficient to fully occur, ensuring the stable existence of TiB_2 particles in the aluminum melt. Under the influence of gravity, the second phases TiB_2 and TiAl_3 generated by the reaction enter the aluminum melt, where TiAl_3 interacted with it due to the presence of rare earths in the melt:



$$\Delta G_4^\theta(\text{Ti}_2\text{Al}_{20}\text{RE}) = -227,024 + 74.837T_4 \quad (14)$$

When the synthesis temperature was 1103.15 K ($830\text{ }^\circ\text{C}$), by calculating (1) $\Delta G_1^\theta(\text{Ti}_2\text{Al}_{20}\text{RE}) = -227,024 + 74.837 \times 1103.15 = -144,467.56345\text{ kJ}\cdot\text{mol}^{-1} < 0$, the result was the production of $\text{Ti}_2\text{Al}_{20}\text{RE}$. When $T_4 \geq 3033.58\text{ K}$ ($2760.43\text{ }^\circ\text{C}$), $\Delta G_4^\theta(\text{Ti}_2\text{Al}_{20}\text{RE}) \geq 0$, the reaction (14) proceeds to the left, $\text{Ti}_2\text{Al}_{20}\text{RE}$ cannot be stabilized, and $\text{Ti}_2\text{Al}_{20}\text{RE}$ decomposed and dissolved, and since the refinement agent synthesis temperature was at atmospheric pressure $830\text{ }^\circ\text{C} < 2760.43\text{ }^\circ\text{C}$, $\text{Ti}_2\text{Al}_{20}\text{RE}$ can be stabilized at $830\text{ }^\circ\text{C}$. According to the free energies, it can be determined that the synthesis temperature of the grain refiner was $830\text{ }^\circ\text{C}$, and each reaction (11)–(14) can proceed to the right.

The Gibbs free energy was the lowest in the chemical reaction for synthesizing $\text{Ti}_2\text{Al}_{20}\text{RE}$, indicating its best stability. According to the Gibbs free energy function of Equation (14), it can be calculated that at a temperature of $T = 1103.15\text{ K}$, $\Delta G = -144,467.56345\text{ kJ}\cdot\text{mol}^{-1}$. The lowest value indicated a very good trend of spontaneous chemical reaction, which was also the fundamental reason why the melt-matching reaction method can significantly reduce production costs. Therefore, the synthesis temperature not only affected the thermodynamic process of the reaction but also caused changes in the composition and structural state of the melt by affecting the stability of the compound and inherited this change into the solid structure. Therefore, when the synthesis temperature was higher than a certain value, the decomposition of certain phases (e.g., TiAl_3 , etc.) occurred, which changed the structure of the melt composition, thus affecting the kinetic process of crystallization.

3.3. Crystallization Kinetics Analysis

The total free energy of the system decreases as the crystal size grows with the growth of the nucleus during the crystallization process. The reaction continues in a direction that is conducive to the growth of the crystal nucleus. The growth of crystal nuclei is considered to be a process in which atoms in the liquid phase migrate to the surface of the crystal nucleus, i.e., the liquid–solid interface advances towards the liquid phase. During the solidification process, there are two types of atomic migration occurring simultaneously at the liquid–solid interface, namely, the migration of atoms from the liquid phase to the solid

phase and the migration of atoms from the solid phase to the liquid phase. If N represented the number of atoms that migrate per unit area in time t , then [30]:

$$R_F = \left(\frac{dN}{dt}\right)_F = A_F G_F N_L \nu_L \exp\left(-\frac{O_F}{\kappa T}\right) \quad (15)$$

$$R_m = \left(\frac{dN}{dt}\right)_m = A_m G_m N_s \nu_s \exp\left(-\frac{O_m}{\kappa T}\right) \quad (16)$$

where R_F —the solidification rate; R_m —melting rate; A_F —the probabilities of liquid-phase atoms reaching the solid phase; A_m —solid-phase atoms reaching the liquid phase and being able to settle (without being bounced back due to collisions); G_F —the probabilities of liquid-phase atoms transitioning to solid phase; G_m —the probabilities of solid-phase atoms transitioning to liquid phase; N_L —the atomic migration numbers per unit area of liquid at the interface; N_s —the atomic migration numbers per unit area of solid phases at the interface; ν_L —the vibrational frequencies of the atoms in the liquid phase; ν_s —the vibrational frequencies of the atoms in the solid phase; Q_F —the activation energies of the atoms for the leaps from the liquid phase to the solid phase; Q_m —the activation energies of the atoms for the leaps from the solid phase to the liquid phase.

If T_i (interface temperature) = T_m (melting point temperature), then $R_F = R_m$, and solidification and melting were in dynamic equilibrium, i.e., the number of atoms that migrated from the liquid phase to the solid phase nucleus was equal to the number of atoms that migrated from the nucleus to the liquid phase, so the nucleus cannot grow. To promote the growth of crystal nuclei, that is, to push the solid–liquid interface into the liquid phase, $R_F > R_m$ was required. The interface temperature T_i that satisfied this condition must be lower than the melting point temperature T_m , that is, there must be a certain dynamic (kinetic) undercooling degree ΔT_k ($\Delta T_k = T_m - T_i$) at the interface. The dynamic undercooling ΔT_k was necessary for achieving net atomic transport from liquid to solid at the interface. And in the supercooled liquid, a large number of phase undulations of varying sizes sprang up every instant. At a certain temperature, the probability of phase fluctuations of different sizes occurring varied. The probability of phase fluctuations occurring in both large and small sizes was small, and there was a limit value $r_{\max}$ for the largest phase fluctuations occurring at each temperature. The size of $r_{\max}$ was related to temperature. The higher the temperature, the smaller the $r_{\max}$ size, and the lower the temperature, the larger the $r_{\max}$ size. The larger phase fluctuations that appeared in supercooled liquids were likely to transform into crystal nuclei during crystallization, and these phase fluctuations were the germ of the crystal nucleus, namely the crystal embryo. The effect of crystal embryo on the crystallization kinetic process is shown by the nucleation rate (I) of the solid phase precipitated from the liquid phase [31]:

$$I = k N_V^P \exp\left[-\frac{16\pi\sigma_{\alpha L}^3 f(\theta)}{3K_b \Delta S^2 \Delta T^2}\right] \quad (17)$$

where I —nucleation rate; k —coefficient of Boltzmann's constant with respect to atomic diffusion; N_V^P —number of nuclei in the melt; $\sigma_{\alpha L}$ —interfacial tension; ΔS —entropy of nucleation; ΔT —supercooling of nucleation.

According to Equation (17), the nucleation rate I was directly proportional to the number of embryos N_V^P in the melt and increased exponentially with the increase in nucleation undercooling ΔT . Therefore, when preparing Al-5Ti-1B-1RE master alloy by the melt-matching method, the solid–liquid interface advanced towards the liquid phase when the solidification rate $R_F > R_m$ melting rate. If the undercooling degree ΔT of nucleation was larger and the critical number of embryos N_V^P was greater, the nucleation rate I was higher, and vice versa. The higher the melt temperature, the smaller the nucleation supercooling ΔT ; the stronger the diffusion of atoms, the smaller phases may merge and grow preferentially; and the smaller the number of critical embryos, the lower the nucleation rate I was.

From the above, it can be seen that when the Al-5Ti-1B-1RE master alloy was prepared by the melt-matching method, the nucleation rate I of the undercooled liquid mainly depended on the thermodynamic nucleation work at higher temperatures (with lower undercooling ΔT), and the activation energy Q of dynamic atomic diffusion became a secondary factor. When the temperature was low (with a large degree of undercooling ΔT), the nucleation rate N mainly depended on the kinetic atomic diffusion activation energy Q , while the thermodynamic nucleation work became a secondary factor. When the temperature was appropriate, there was a certain degree of undercooling ΔT , and the thermodynamic nucleation rate I_1 and the dynamic nucleation rate I_2 had an optimal combination. At this point, the nucleation rate I reached its maximum value, and a “peak” appeared on the nucleation rate curve, as shown in Figure 6, which was inherited into the solid structure.

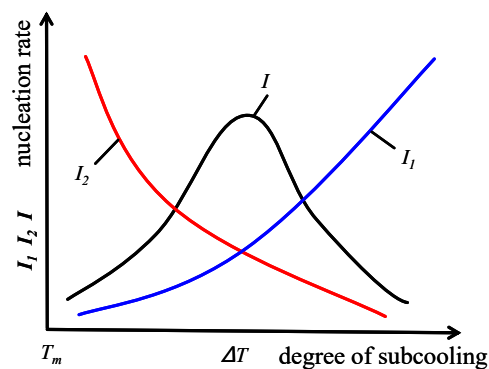


Figure 6. Relationship curve between nucleation rate I and undercooling ΔT .

3.4. Refinement Analysis of Different Grain Refiners

3.4.1. Analysis of Refining Effects of Different Grain Refiners

The self-made Al-5Ti-1B-1RE master alloy grain refiner was used to refine commercial pure aluminum in comparison with the home-made Al-Ti-B wire and the Al-Ti-B wire master alloy grain refiner manufactured by the British company LSM under the same refining test conditions. The OM photos are shown in Figure 7. The photos are taken from the center position of each metallographic specimen. The unrefined pure aluminum microstructure was coarse columnar crystals with hardly a single intact grain placed in the field of view, as shown in Figure 7a. The grain size of commercial pure aluminum was significantly reduced by the master alloy grain refiner. When adding domestic Al-Ti-B wire master alloy grain refiner, most of them were equiaxed crystals, but there were still a considerable number of coarse grains, with an average grain diameter of 95.6 μm . And some of the grains had sharp corners, which was detrimental to the mechanical properties of refined pure aluminum and displayed a weakening effect. In the green circles in Figure 7b, the grains indicated by the red arrows had obvious sharp corners. When the imported Al-Ti-B wire master alloy was added, its grain size was smaller than that of the domestic Al-Ti-B wire master alloy refiner added in equal amount, but the grain size was still somewhat uneven, with an average grain diameter of 64.7 μm , and there were few grains with sharp corners in the grains. This indicates that the effect of imported Al-Ti-B wire master alloy was better than that of domestic Al-Ti-B wire master alloy, and its refinement effect is shown in Figure 7c. When the self-made Al-5Ti-1B-1RE master alloy grain refiner was added, the grain size was significantly refined, and most of them had been transformed into fine equiaxed crystals. The grain size was smaller than that of domestic and imported Al-Ti-B wire master alloy grain refiner, and the average grain diameter was 50.2 μm . There was an obvious advantage in the refining effect and grain uniformity, as shown in Figure 7d. The commercial pure aluminum refined by the self-made Al-5Ti-1B-1RE master alloy grain refiner had rounded grains, close to the equiaxed grain shape, with little cutting effect on

the matrix, and its high level of refinement was assessed to have reached the fine grain level in terms of average grain diameter [32].

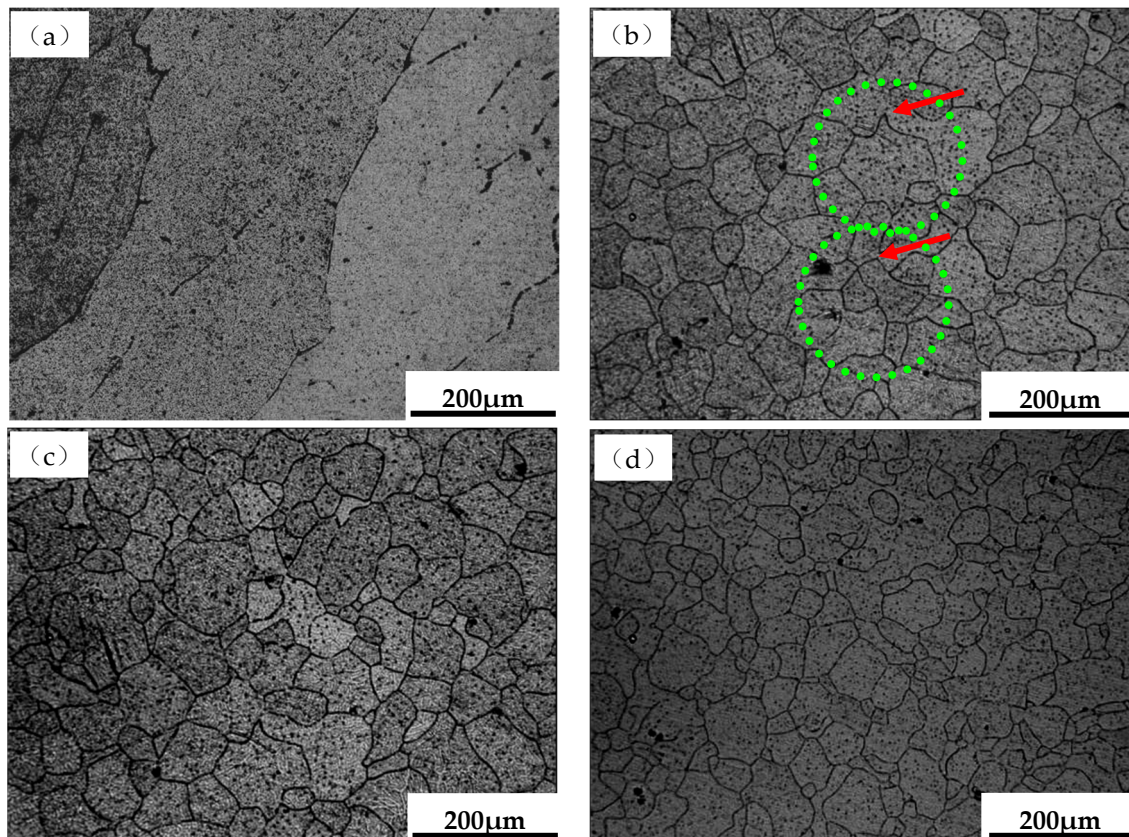


Figure 7. Comparison about refining effect of different kinds of refiners: (a) pure aluminum unrefined; (b) Al-5Ti-1B master alloy made in our country; (c) Al-5Ti-1B master alloy imported; (d) Al-5Ti-1B-1RE master alloy refiners.

3.4.2. Analysis of Refining Properties of Different Grain Refiners

The mechanical tensile properties tests were carried out on commercial pure aluminum refined by different refiners. Unrefined commercial pure aluminum, domestic and British LSM produced Al-Ti-B wire master alloy refiners and homemade Al-5Ti-1B-1RE master alloy refiners refined commercial pure aluminum were marked as a, b, c, and d, respectively. And the tensile strength σ_b and elongation of each tensile specimen were measured. From the test results of tensile properties of the specimens, as shown in Figure 8, it can be seen that the tensile strength σ_b and elongation of specimens a, b, c, and d increased in order. And their tensile strength σ_b was 53.00 MPa, 67.00 MPa (26.42% higher than pure aluminum σ_b), 69.26 MPa (30.68% higher than pure aluminum σ_b), and 75.00 MPa (41.51% higher than pure aluminum σ_b), respectively. The tensile strength σ_b of d was increased by 11.94% and 8.29% compared to specimens b and c, respectively. The elongation rates at break δ were 23.38%, 39.20% (increased by 67.59% compared to pure aluminum δ), 44.00% (increased by 88.54% compared to pure aluminum δ), and 51.66% (increased by 120.96% compared to pure aluminum δ), respectively. The elongation δ of d increased by 31.79% and 17.41% compared to a and b, respectively. The tensile strength σ_b and elongation of specimens b, c, and d were increased compared to the a specimen's tensile, especially specimen d was significantly increased, which also corresponded to the effect of different types of master alloy refiners refining in Figure 7.

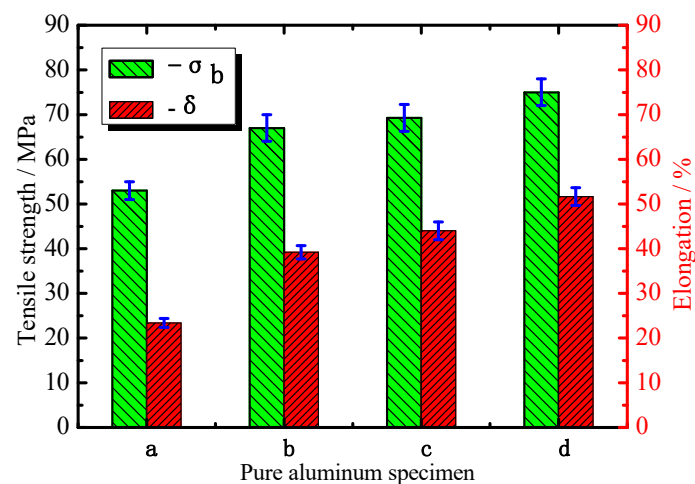


Figure 8. The mechanical properties of pure aluminum before and after adding different grain refiners: a—the pure Al unrefined; b—adding Al-Ti-B made in our country; c—adding Al-Ti-B imported; d—adding self-made Al-5Ti-1B-1RE refiners.

The grain size directly determined the mechanical properties of aluminum and aluminum alloys. The level of mechanical properties also directly reflected the degree of grain refinement, as expressed by the Hall Petch formula [33]:

$$\sigma = \sigma_0 + Kd^{-1/2} \quad (18)$$

where σ_0 —constant, represents the resistance to deformation within the crystal, which is approximately 2–3 times the critical shear stress in the slip direction of a single crystal on the slip plane; K —constant, characterizes the influence of grain boundaries on deformation, which depends on the structure; d —grain size.

According to Equation (18), the tensile strength σ of polycrystalline materials is linearly related to the reciprocal of the square root of their grain diameter d , and the smaller the grain size, the higher the strength. This indicates that with the addition of grain refiners to commercial pure aluminum, the number of non-spontaneous nucleation of its second phase particles increases significantly, effectively promoting nucleation and grain refinement. The smaller the grain size, the more grain boundaries there are, and the greater the deformation resistance, the higher the macroscopic tensile strength. On the other hand, under the same external force, the smaller the grain size, the more uniform the deformation of each grain, and the lower the probability of stress concentration. Cracks are less likely to initiate and propagate and can withstand a larger amount of deformation before fracture, resulting in higher macroscopic plasticity. When using self-made Al-5Ti-1B-1RE master alloy to refine pure aluminum, a large number of effective second-phase nucleation particles were released in a short period of time, generating new nucleation particles before the growth of the melt, hindering the growth of columnar crystals, and changing the crystal growth morphology towards fine equiaxed crystals, promoting grain refinement and improving the toughness of the materials. The mechanical properties of pure aluminum refined by adding self-made Al-5Ti-1B-1RE master alloy were significantly better than those of commercial pure aluminum refined by adding an equal amount of Al-5Ti-1B wire mater alloy, as shown in Figure 7. In addition, the presence of inclusions, impurities, or gases in the commercial pure aluminum melt can lead to the presence of various defects in the crystals, such as porosity, which significantly reduced the overall performance of commercial pure aluminum [34]. However, the RE element itself has the function of purifying aluminum melt, significantly reducing impurities and defects such as pores in pure aluminum, and improving mechanical properties. Therefore, specimen d has the smallest grain size and the highest tensile strength σ_b and elongation.

3.4.3. Analysis of Refinement Mechanism of Al-5Ti-1B-1RE Master Alloy

As the second phase of Al-5Ti-1B-1RE master alloy is mainly TiAl_3 , TiB_2 , and $\text{Ti}_2\text{Al}_{20}\text{RE}$, when added to the commercial pure aluminum melt, TiAl_3 quickly dissolved. TiB_2 had a high melting point of 2980 °C and still existed in solid form in the melt. TiB_2 and TiAl_3 in the melt had good wettability due to their small wetting angle. The planes formed by the strong covalent bond network of B–B in the TiB_2 crystal structure provided the possibility for TiAl_3 to nucleate on its surface. Therefore, Ti preferentially formed a Ti-rich layer around TiB_2 particles, with TiB_2 particles as the center and TiAl_3 forming around TiB_2 , as shown in Figure 9a,b, in the areas indicated by red arrows A and B. The energy spectrum region scanning analysis was carried out, which mainly contained Al, Ti, B, and a small amount of RE, as shown in Figure 9c. Combined with the X-ray diffraction results in Figure 3 and the morphological characteristics of the second-phase particles in the Al-5Ti-1B-1RE master alloy, it can be determined that the central black particle material was TiB_2 , and the phases surrounding TiB_2 were mainly TiAl_3 and rare-earth phases. Ti formed a TiAl_3 coating layer, namely $\text{Ti} + 3\text{Al} \rightleftharpoons \text{TiAl}_3$. During the solidification process, a large amount of TiB_2 wrapped in a thin layer of TiAl_3 served as an effective nucleation substrate for α -Al, promoting nucleation and refining the α -Al grains [35].

Simultaneously conducting point scanning analysis on points C and D in Figure 9a, it was found that regions A and B have the same analysis results. On the other hand, the RE element released by the dissolution of the second-phase particle $\text{Ti}_2\text{Al}_{20}\text{RE}$ phase forms a protective thin layer on the surface of TiAl_3 , i.e., $\text{Ti}_2\text{Al}_{20}\text{RE} \rightleftharpoons 14\text{Al} + 2\text{TiAl}_3 + \text{RE}$, and the energy spectrum analysis of the E and F regions in Figure 9b is shown in Figure 9d, in which the E grey region mainly contained the two elements of aluminum and titanium, and its atomic percentage content ratio was $\text{Ti}:\text{Al} \approx 1:3$, it can be determined that the substance was TiAl_3 . The white region of phase F, which surrounds the bulk TiAl_3 phase E, was then analyzed by energy spectroscopy to contain Ti, Al, and RE with an atomic percentage ratio of $\text{Ti}:\text{Al}:\text{RE} \approx 2:20:1$, as shown in Figure 9e. Combined with the results of X-ray diffraction in Figure 3, it can be judged to be the $\text{Ti}_2\text{Al}_{20}\text{RE}$ phase with a complex face-centered cubic structure. At the same time, due to the release of RE atoms from the $\text{Ti}_2\text{Al}_{20}\text{RE}$ phase surrounding TiAl_3 , which was partially converted into TiAl_3 phase to promote the formation of TiAl_3 on the surface of TiB_2 , the TiAl_3 phase can exist in the aluminum melt for a longer period of time and the refining effect lasted for a longer period of time, which protected the formation of TiAl_3 on TiB_2 grains, i.e., it further promoted nucleation and α -Al grain refinement, as shown in the schematic diagram of the dual nucleation theory in Figure 10, which was consistent with the dual nucleation refinement theory proposed by P.S. Mohanty et al. [36].

In addition, the rare-earth elements themselves played a positive role in refining pure aluminum, with a portion of the rare-earth elements being pushed up to the grain boundaries during the solidification process. Due to the RE atomic radius of 0.174–0.204 nm, which was larger than the aluminum atomic radius of 0.143 nm, and the solid solubility in aluminum being extremely low, the precipitation of rare-earth elements caused α -Al lattice distortion, with a strong pinning of grain boundaries and sub granular boundaries, which played a role in refining the grain.

The other part of rare-earth elements mainly played a role in promoting the protection of the dual nucleation of the TiAl_3 and TiB_2 phases during the refinement process. To obtain a good refining effect, in the synthesis and preparation of Al-5Ti-1B-1RE master alloy ensure that TiB_2 is in the mass ratio of $\frac{\text{Ti}}{\text{B}} > \frac{47.867}{2 \times 10.811} = 2.21$, that is, in addition to the generation of TiB_2 , the Ti mass had a surplus, the generation of TiAl_3 , which was a prerequisite for obtaining effective nucleation of the TiAl_3 phase and TiB_2 phase. The self-made Al-5Ti-1B-1RE master alloy with $\frac{\text{Ti}}{\text{B}} = \frac{5}{1} > 2.21$ can obtain effective nucleation and a better refinement effect.

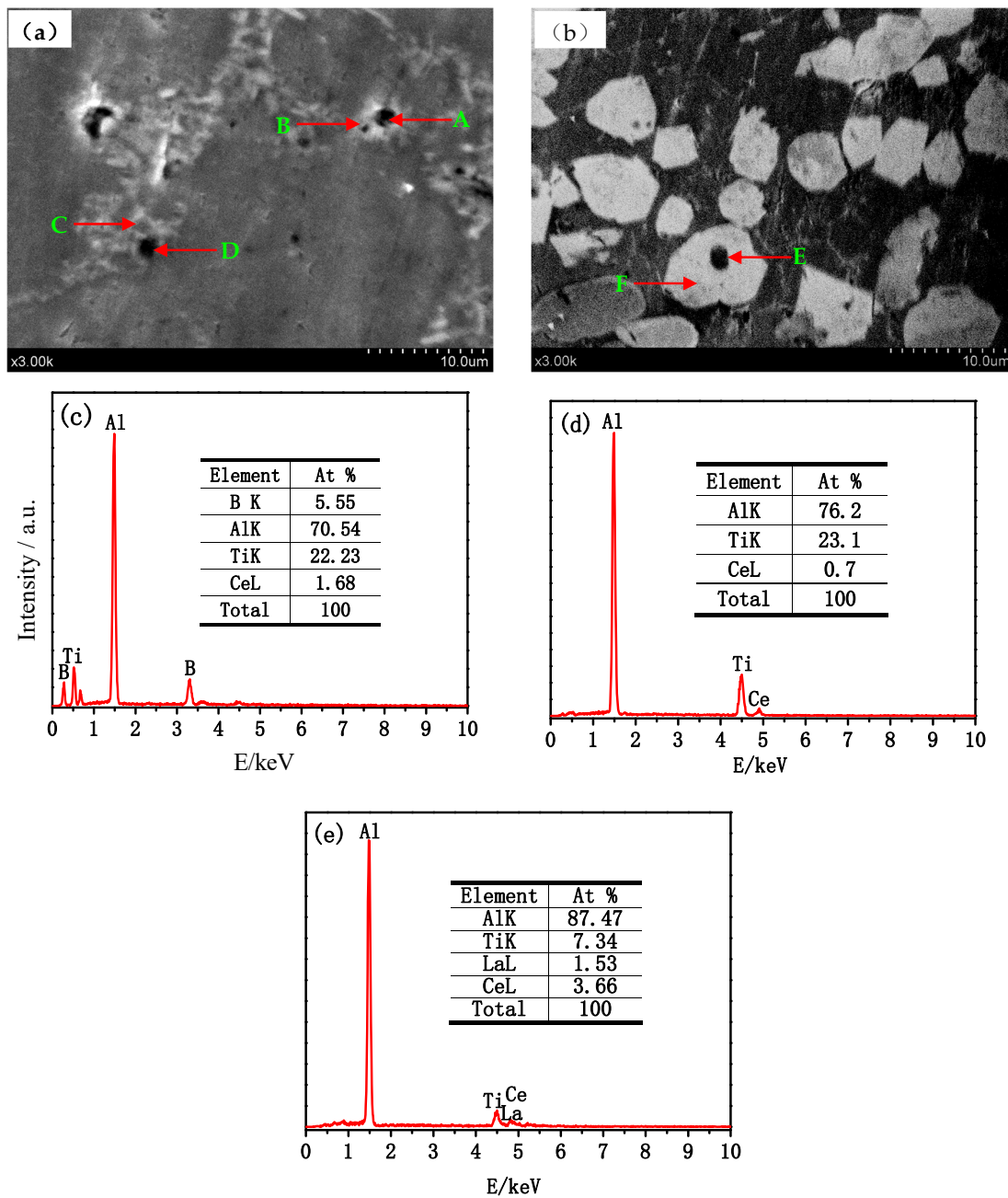


Figure 9. SEM micrographs of nucleus and EDS analysis results: (a) SEM of the secondary phase of Al-5Ti-1B-1RE; (b) EDAX of A, B; (c) SEM of the secondary phase of Al-5Ti-1B-1RE; (d) EDAX of E; (e) EDAX of F.

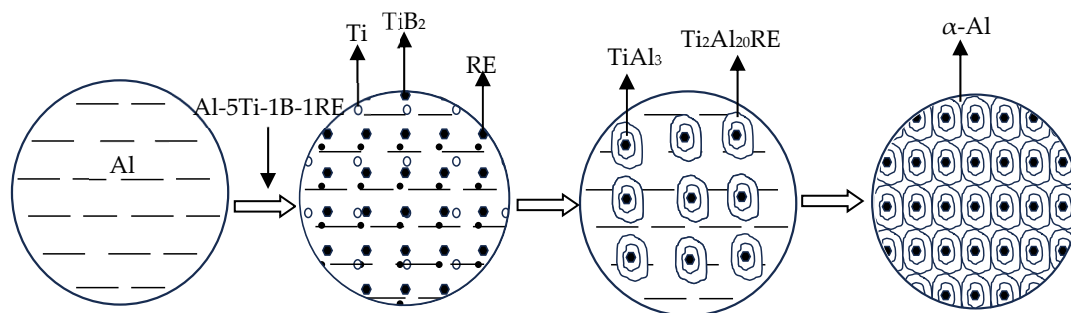


Figure 10. Schematic diagram of the duplex nucleation theory.

4. Conclusions

1. When synthesizing a new Al-5Ti-1B-1RE master alloy grain refiner by the melt-matching method, the reaction generated by the second-phase TiB_2 and TiAl_3 in the aluminum melt had an interaction with TiAl_3 due to the presence of rare earths in the melt: $14\text{Al} + 2\text{TiAl}_3 + \text{RE} = \text{Ti}_2\text{Al}_{20}\text{RE}$.
2. When the new Al-5Ti-1B-1RE master alloy grain refiner was synthesized by the melt-matching method at a synthesis temperature of 1103.15 K (830 °C), it was calculated that the magnitude of Gibbs free energy ΔG was $\Delta G_{\text{Ti}_2\text{Al}_{20}\text{RE}} < \Delta G_{\text{TiB}_2} < \Delta G_{\text{Al}_3\text{Ti}}$.
3. When the temperature was appropriate, there was a certain degree of subcooling ΔT , and the thermodynamic nucleation rate I_1 and the kinetic nucleation rate I_2 had an optimal fit, at which time the nucleation rate I reached the maximum value and a “peak” appeared on the nucleation rate curve.
4. The mechanical properties of pure aluminum refined by Al-5Ti-1B-1RE master alloy were significantly better than those of pure aluminum added with equal amounts of domestic and imported Al-5Ti-1B wire master alloy. The tensile strength σ_b was increased by 11.94% and 8.29% and the elongation δ by 31.79% and 17.41%, respectively.
5. Due to the addition of RE elements, the refining effect lasts longer. The refining mechanism of Al-5Ti-1B-1RE master alloy for commercial pure aluminum was a dual nucleation refining mechanism.

Author Contributions: Conceptualization, Z.W. and S.W.; methodology, Z.W.; validation, S.W. and X.L.; formal analysis, Q.Y.; investigation, Q.Y. and L.L.; resources, S.W.; data curation, C.D.; writing—original draft preparation, Z.W. and S.W.; writing—review and editing, Z.W. and S.W.; supervision, X.L. and L.L.; funding acquisition, Z.W., Q.Y., and C.D.; All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Natural Science Foundation of China, No. 52104375, Major Project of Basic Science (Natural Science) Research of Institution of Higher Education of Jiangsu Province, China, No. 22KJA460010, Huai'an Science and Technology Bureau Project, Jiangsu Province, China, No. HABL202206.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: There are no conflicts of interest to declare.

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