https://doi.org/10.1007/s41230-021-9021-5

Effect of Gd on microstructure and refinement performance of Al-5Ti-B alloy

***Dong-song Yin[1], Ning Zhang[1], Ke-ju Chen[1], **Yun-long Zhang[2]**

1. School of Materials Science and Engineering, Heilongjiang University of Science and Technology, Haerbin 150022, China

2. School of Materials Science and Engineering, Jiamusi University, Jiamusi 154007, China

Abstract: Al-5Ti-B and Al-5Ti-B-Gd master alloy refiners were fabricated by fluorine salt casting method. The microstructure and phase constitution of the master alloys were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The results show that Al-Ti-B alloy refiner consists of Al_3Ti phase and TiB_2 phase. After Gd is introduced into the intermediate alloy, $Ti_2Al_{20}Gd$ phase appears in the alloy, the size of Al_3Ti is significantly reduced, and Ti-Al-Gd phase is found in the edge of Al_3Ti phase. At the same time, some independent Ti-Al-Gd phases appear in local areas, which are $Ti_2Al_{20}Gd$ phase determined by micro-area electron diffraction analysis. Analysis and calculation results of the high-resolution images of the $Ti_2Al_{20}Gd$/Al structure show that there is no other compound at the junction between the $Ti_2Al_{20}Gd$ phase and Al, and $Ti_2Al_{20}Gd$ phase has a great difference in atomic space with the α-Al, which cannot be directly used as heterogeneous nucleus. But, after being decomposed in the aluminum melt, the $Ti_2Al_{20}Gd$ phase can promote the refinement effect of the refiner. In the Al-Ti-B-Gd master alloy, there are many dispersed Al_3Ti particles with a size of less than 1 μm, which can promote the Al-5Ti-B refining effect.

Key words: Al-5Ti-B alloy refiner; Al_3Ti; rare earth Gd; $Ti_2A1_{20}Gd$

CLC numbers: TG146.21 **Document code:** A **Article ID:** 1672-6421(2021)03-223-06

1 Introduction

Aluminum alloys have the advantages of low density, high specific strength, good ductility and easy recycling. As structural materials, they are widely applied in the fields of aerospace, automobiles, electronics and rail transportation. However, the coarse grain of as-cast aluminum alloy reduced the mechanical properties and significantly reduced the subsequent rolling properties. To solve this problem, the most common method in industry is to introduce Al-Ti-B refiner to obtain fine equiaxed grains, with the aim to improve the comprehensive mechanical properties and calendering ability of aluminum alloy [1-2].

The synthetic method of Al-Ti-B grain refiner was mainly a fluoride salt method. However, the potassium fluoroaluminate, as by-product, is adulterated into the Al-Ti-B grain refiner, which reduces the purity of the Al-Ti-B grain refiner, and therefore, leads to a significant decrease in the mechanical properties and corrosion resistance of aluminum alloys. The most important is that the coarse needle-like and strip-like Al_3Ti existing in the Al-Ti-B deteriorates its refining performance. Many researchers reported that the size and morphology of Al_3Ti particles had obvious influence on the refining capacity of Al-Ti-B refiner [3]. Researchers adopted different strategies to control the size and morphology of Al_3Ti particles, such as ultrasonic technology, mechanical or electromagnetic stirring, and so on. However, the action scope of ultrasonic method is narrow, and it is difficult to realize industrialization. Mechanical and electromagnetic stirring methods require special equipment, so the production cost is high. In addition, the oxidation inclusions are easy to be involved during the operation process, thus reducing the refining performance of Al-Ti-B refiner [4–5].

The addition of rare earth elements to aluminum alloys has unique advantages. An appropriate amount of rare earth elements (La Ce Er Y, etc.) can purify the melt of Al-Ti-B alloy and significantly increase the long-term effectiveness of the refiner. Rare earth elements have a unique activity, which can significantly affect the morphology, size, and

***Dong-song Yin**

Male, born in 1974, Ph. D., Professor. His research interest mainly focuses on light alloys. To date, he has published 40 technical papers and 2 books, and holds 5 invention patents of China.

E-mail: dongsongyin@126.com

***Yun-long Zhang**

E-mail: ylzhdr@126.com

Received: 2020-12-08; Accepted: 2021-03-25

distribution of the second phase in the metal, and can also have a significant impact on the refining effect of the alloy refiner [1-3]. Reports showed that rare earth could refine Al_3Ti phase and form $Ti_2Al_{20}Re$ phase, which significantly improved the refining performance of alloy refiners [4-7]. However, there is a lack of in-depth research on the in-situ crystallographic diffraction analysis of $Ti_2Al_{20}Re$ phase and the interface relationship between $Ti_2Al_{20}Re$ and aluminum matrix, which will affect the judgment of the refining effect of $Ti_2Al_{20}Re$ on aluminum alloy. Yin et al. [8] found that Gd element can significantly improve the refinement effect of Al-5Ti on Al-7Si alloy, but the mechanism of how Gd element affected the Al_3Ti phase was unclear.

In this study, Al-5Ti-B refiner was prepared by fluoride salt method. The microstructure of the alloy after adding Gd was observed. The influence of rare earth Gd on heterogeneous nucleation particles in the refiner was discussed. It would provide a reference for the research and development of Al-Ti-B refiner containing rare earth elements.

2 Experimental procedure

Industrial double zero aluminum (≥99.70%), titanium powder (≥99.50%) and potassium fluoborate (≥98.00%) were utilized as raw materials, and rare earth Gd was added in Al-30%Gd intermediate alloy. The aluminum ingot was put into a graphite crucible (a well-type resistance furnace), and heated to (850±5) °C. After the aluminum melt was completely melted, titanium powder and KBF_4 which have been crushed into pieces were added into the melt using a graphite bell jar. After the reaction was accomplished, Al-30%Gd master alloy was added, then slag was removed with stirring, and then cooled to 800 °C. Finally, it was cast into a metal mold to obtain the aluminum alloy refiner containing rare earth elements. The metal mold had an inner diameter of 50 mm to obtain a cylindrical refiner with a size of Φ50 mm×50 mm. The process was carried out under special covering agent, degassing agent and refining agent for aluminum alloys.

Block samples of 10 mm×10 mm×10 mm were cut from the center of the cylindrical Al-5Ti-1B and Al-5Ti-1B-1Gd master alloy refiners. Part of the sample was cut off, ground and polished, then eroded with reagent (95.5 mL H_2O+0.5 mL HF). The phase constitution of the alloy was analyzed using a Bruker DS Advance X-ray diffractometer. The microstructure was observed using a QUAN200 scanning electron microscope (SEM), and the composition of the micro-area was analyzed using an energy dispersive analyzer (EDS). The morphology of solidified phase was analyzed using the FEI Talos field emission transmission electron microscopy (TEM).

3 Results and discussion

3.1 Phase constitution

Figure 1 shows the X-ray diffraction patterns of Al-Ti-B and Al-Ti-B-Gd master alloy refiners. It can be seen that the diffraction pattern of Al-Ti-B alloy refiners has not only many α-Al diffraction peaks, but also $A1_3Ti$ and TiB_2 diffraction peaks.

The following reactions take place when titanium powder briquette and potassium fluoborate briquette are added at the same time to prepare Al-Ti-B:

$$L \rightarrow Al + Al_3Ti \quad (1)$$

$$2KBF_4 + 3Al \rightarrow AlB_2 + 2KAlF_4 \quad (2)$$

$$AlB_2 + Al_3Ti \rightarrow TiB_2 + 4Al \quad (3)$$

For Al-Ti-B-Gd master alloy, besides the above diffraction peaks, there is also a diffraction peak of $Ti_2A1_{20}Gd$ phase. This is because the rare earth Gd elements react with Al_3Ti when they are enriched to a certain concentration [7]:

$$14Al + 2A1_3Ti + Gd \leftrightharpoons Ti_2A1_{20}Gd \quad (4)$$

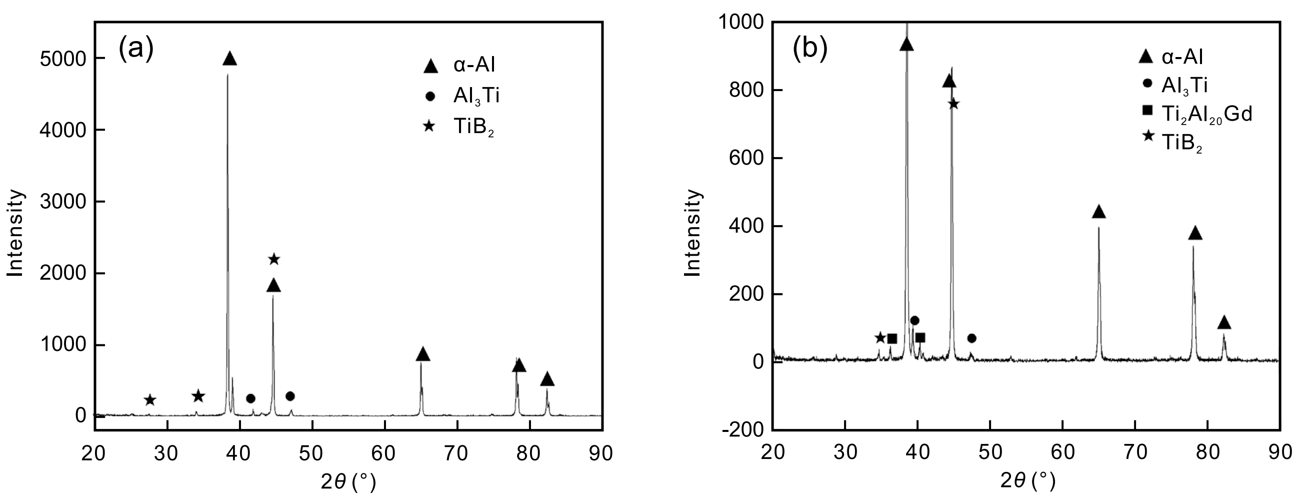

Fig. 1: X-ray diffraction patterns of Al-Ti-B (a) and Al-5Ti-B-Gd alloy (b)

3.2 Microstructure

Figure 2 shows the SEM of Al-5Ti-B and Al-5Ti-B-Gd master alloys. It can be seen in Fig. 2(a) that there are coarse and irregularly shaped solid phases [such as Area A in Fig. 2(a)] distributed in the alloy matrix, and their sizes fluctuate within the range of 20–100 μm. The results of energy spectrum analysis at Area A show that this phase is Al-Ti phase, and the molar ratio of Al/Ti is close to 3:1 (Table 1). Combined with X-ray diffraction analysis and previous research [5-7], this phase can be determined as Al_3Ti. After adding rare earth Gd, as shown in Fig. 2(b), the solid phase is refined and distributes dispersively, with significant changes in morphology. As shown in the lower left corner of Fig. 2(b), there is a solidified structure with unique morphology, which is composed of Phase C with bright white edge contrast and Phase B with dark gray center contrast. According to energy spectrum analysis, Phase C is TiAlGd and Phase B is Al-Ti. The Ti/Al/Gd molar ratio of the TiAlGd phase is close to 2:20:1; the Al/Ti molar ratio of Al-Ti phase is close to 3:1 (as shown in Table 1). Therefore, it is speculated that Phase C is $Ti_2A1_{20}Gd$ and Phase B is Al_3Ti. This kind of structure has also been found when adding rare earth elements such as Ce and La to the Al-Ti-B alloy [5]. However, few reports can be found concerning the $Ti_2A1_{20}Gd$ phase that is produced by adding Gd to Al-5Ti-B alloy. The in-situ analysis and verification on $Ti_2A1_{20}Gd$ phase were carried out by electron diffraction as shown below.

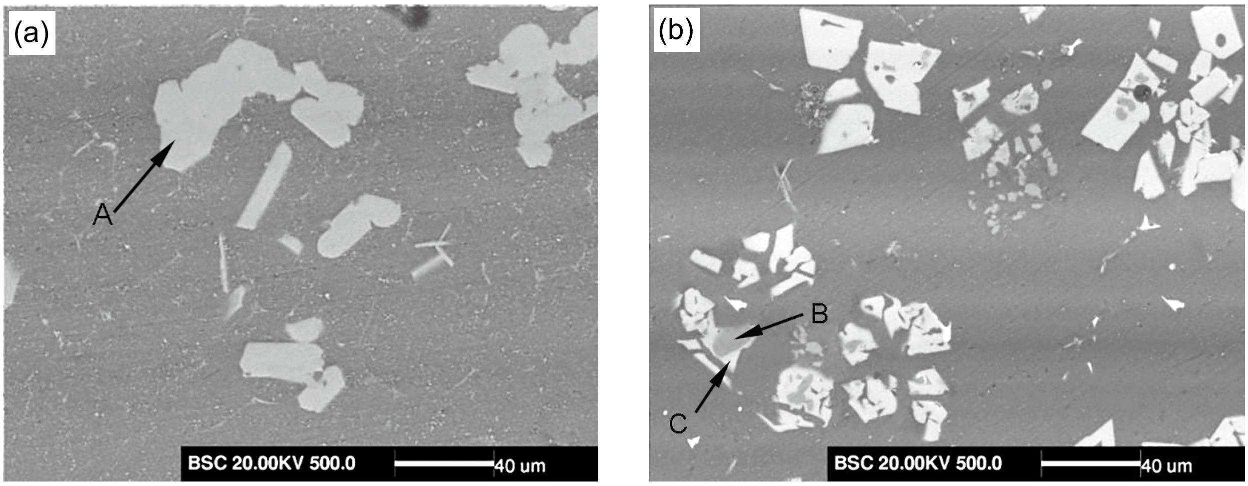

Fig. 2: SEM morphology of Al-5Ti-B and Al-5Ti-1B-Gd master alloy: (a) Al-5Ti-1B; (b) Al-5Ti-1B-Gd

Figure 3(a) shows the microscopic morphology of the Al-5Ti-B-Gd master alloy. There are two kinds of phases distributed in the alloy matrix, which are accompanied by each other, among which the long block phase in bright gray (Phase D) is Al-Ti, according to the energy spectrum analysis results shown in Table 1, and the dark gray phase (Phase E) is Ti-Al-Gd phase. Combined with XRD results, it was considered that Phase D is Al_3Ti phase and Phase E is $Ti_2A1_{20}Gd$ phase. There are no voids, cracks, and other compound layers at the interface between the above two phases.

The electron diffraction analysis of Point E is carried out and the calibration results of the electron diffraction spots are shown in Fig. 3(b), which indicates that Phase E is $Ti_2A1_{20}Gd$. The calculated lattice constant "a" of this phase is 14.60, which is very close to the lattice constant of $Ti_2A1_{20}Gd$ phase. The above results confirm the existence of $Ti_2A1_{20}Gd$ phase around Al_3Ti phase according to the crystallographic point of view, which is of great significance.

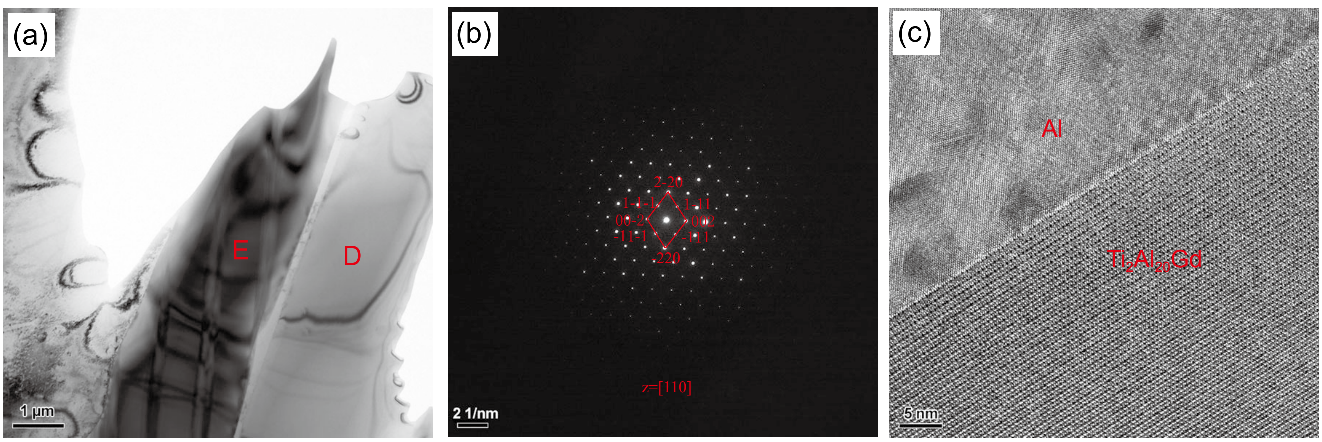

Fig. 3: TEM morphology and electron diffraction analysis of Al-5Ti-1B-Gd master alloy: (a) TEM image; (b) electron diffraction analysis; (c) $Ti_2Al_{20}Gd$/Al high resolution image

Table 1: EDS analysis results of Al-5Ti-1B and Al-5Ti-1B-Gd master alloys (at.%)

Phase	Al	Ti	B	Gd
A	73.64	26.36		
B	73.05	26.95		
C	86.40798	9.20516		4.38686
D	77.51385	22.48615		
E	87.48280	8.26016		4.25705
F	0.91131	21.29957	77.78913	
G	75.42526	24.57474		

Figure 3(c) shows a two-dimensional atomic high-resolution photograph of α-Al and $Ti_2Al_{20}Gd$. After measurement, the single-row atomic spacings of α-Al and $Ti_2Al_{20}Gd$ are 0.2744 nm and 0.9882 nm, respectively, and their interface is in a non-coherent state with a great mismatch degree. Therefore, it can be judged that $Ti_2Al_{20}Gd$ cannot be directly used as heterogeneous nuclei of α-Al.

It can be seen from the above results that $Ti_2Al_{20}Gd$ phase is easy to appear at the edge of Al_3Ti, and the size of $Ti_2Al_{20}Gd$ at the edge of Al_3Ti in different regions is quite different. The reason is that rare earth elements belong to surface active substances and their solid solubility in aluminum melt is extremely low, so they easily aggregate on the adsorption phase interface [10]. With the enrichment of Gd element, $Ti_2Al_{20}Gd$ phase gradually forms and grows, so Ti atoms and Al atoms grow from two sources: one source is diffused from aluminum alloy melt, the other is obtained by consuming Al_3Ti phase. The diffusion and enrichment of Gd element around Al_3Ti creates vital conditions for the nucleation and growth of $Ti_2Al_{20}Gd$. The enrichment degree directly affects the relative size between $Ti_2Al_{20}Gd$ and Al_3Ti. When the growth of $Ti_2Al_{20}Gd$ uses up the Al and Ti atoms in Al_3Ti, a single $Ti_2Al_{20}Gd$ phase appears.

Figure 4(a) shows the fine particle phases distributed in Al-5Ti-B-Gd. It can be found that the hexagonal particle phase F has a size ranging from 50 nm to 200 nm. According to the energy spectrum analysis, this phase mainly contains Ti and B elements [Fig. 4(b)], which can be confirmed as a boride. Its morphology is very similar to that of TiB_2 phase in the matrix of Al-5Ti-B alloy prepared by the fluorine salt method reported in the literature [11,12]. By EDS and XRD analysis (Fig. 1 and Table 1), combined with previous studies, it is speculated to be TiB_2 phase. Generally, Al-5Ti-B master alloy (by fluoride salt method) would have TiB_2 agglomeration phenomenon, that is, TiB_2 phase with coral agglomeration, which decreases the refining effect of the master alloy on the corresponding aluminum alloy [11,12,13]. After the addition of rare earth Gd, this tendency is obviously suppressed, which may be due to that the Gd atoms tend to converge at the interface front of TiB_2 phase, hindering the agglomeration of TiB_2 phase. TiB_2 is a more stable phase in Al-Ti-B than Al_3Ti, which does not react with rare earths [14,15]. Phase G is strip-shaped, containing Al and Ti elements [Fig. 4(c)] with a molar ratio of Al/Ti close to 3:1 (Table 1) from the energy spectrum analysis, so, it is Al_3Ti phase. It did not grow up during the solidification of Al-5Ti-B.

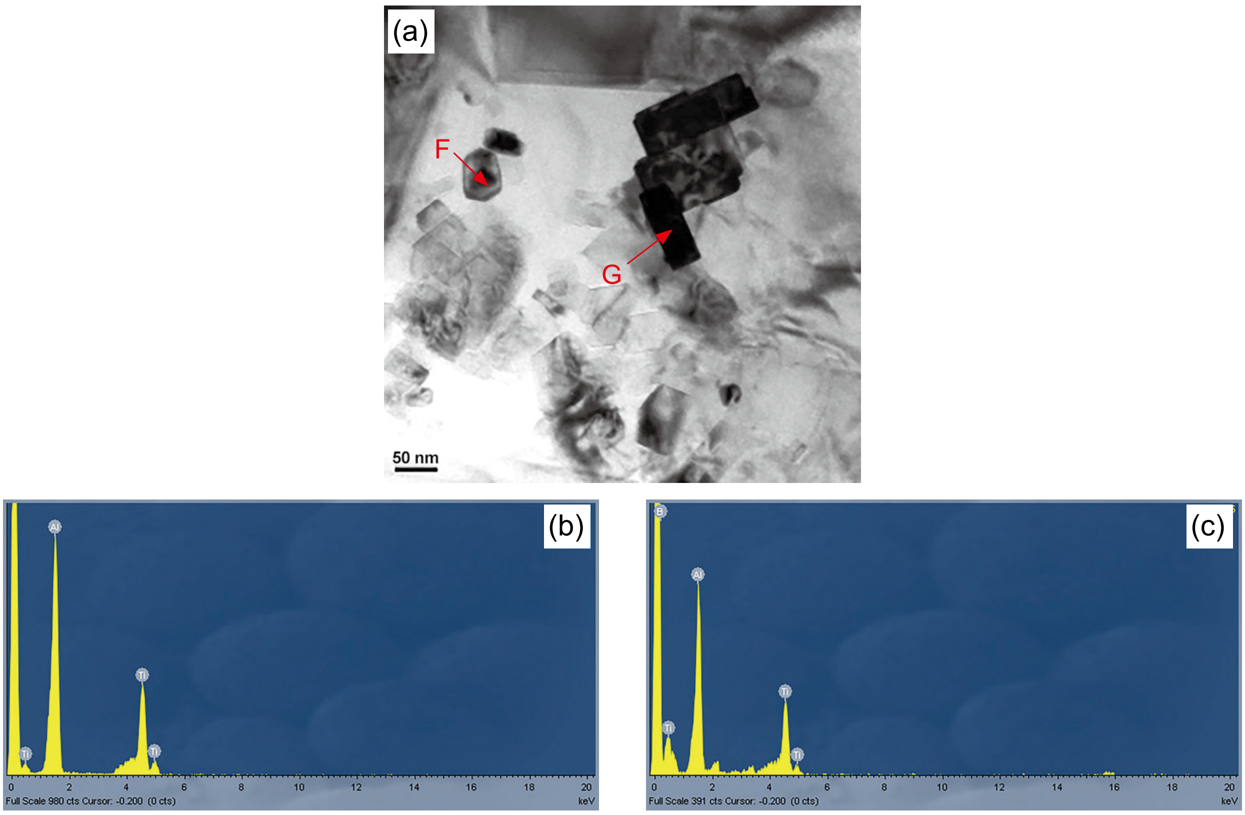

Fig. 4: Morphology and energy spectrum analysis of particle phase in Al-5Ti-B-Gd alloy: (a) particle phase morphology in Al-5Ti-B-Gd alloy; (b) Phase F energy spectrum analysis diagram; (c) Phase G energy spectrum analysis diagram

3.3 Refinement mechanism

This study shows that rare earth Gd can significantly refine Al_3Ti and cause Al_3Ti to be equiaxed, which is one of the main reasons for improving the refining effect of Al-5Ti-B master alloy. According to the phase diagram of Al-Ti binary alloy [16], when Ti content is 0.15% and temperature is 665 °C, peritectic reaction occurs as follows: L+Al_3Ti→α-Al. Al_3Ti is a heterogeneous nucleus of α-Al, which plays a role in refining aluminum alloy. In fact, the final grain size of aluminum alloy is determined by the solute constraint of crystal nucleus and grain growth [16], and the average grain size can be described as:

$$D = a+b/Q \quad [17] \tag{5}$$

where a and b are constants and Q is a growth limiting factor used to measure the influence of solute on grain size when the interaction between solutes is not considered:

$$Q=C_0m(k-1) \quad [17] \tag{6}$$

where C_0 is the solute concentration in the melt, m is the slope of liquidus, k is the equilibrium partition coefficient. The Q value of large flaky Al_3Ti particles is smaller than that of fine flaky Al_3Ti particles, therefore, it can be determined that fine equiaxed Al_3Ti particles have a better refining effect on α-Al than large flaky Al_3Ti particles [17].

After adding Gd element into Al-Ti-B master alloy, the size of Al_3Ti particles is significantly reduced [4-7]. The possible reasons are summarized below: first, the enrichment of rare earth Gd atoms on the surface of Al_3Ti particles hinders the growth of Al_3Ti particles, promotes the dispersion of Al_3Ti particles and prevents their aggregation [5, 6]; second, when Gd atoms are highly enriched, $Ti_2Al_{20}Gd$ phase would form at the edge of Al_3Ti particles, then the $Ti_2Al_{20}Gd$ phase consumes Ti atoms in Al_3Ti, thus, Al_3Ti particles diminish constantly.

Thermodynamically, the $Ti_2Al_{20}Gd$ phase is unstable. At the high temperature, the reaction of $Ti_2Al_{20}Gd \leftrightharpoons 14Al+2Al_3Ti+Gd$ occurs and releases rare earth element Gd. Gd combined with the active contacts on the second phase particles to form a "rare earth film", and the free energy of particles is reduced, so that the particles can exist in the solution for a longer time to play the role of heterogeneous nucleus and thus the refiner has a long-term refinement effect. In addition, the existence of rare earth element film hinders the aggregation and growth of second phase particles, further promoting the refinement ability of refiners [18]. Some rare earth atoms would be released from the rare earth film, although they are not enough to form a compound with the aluminum matrix, they can be concentrated at the boundary between grains and dendrites and play a role in refining grains and dendrites.

In the aluminum alloy, the refining effect of TiB_2 particles alone on α-Al is not obvious. This is because the interface energy of Al/TiB_2 produced by heterogeneous nucleation of α-Al on TiB_2 particles is greater than the liquid-solid interface energy as α-Al nucleates directly from Al melt when aluminum alloy solidifies, so, TiB_2 particles cannot act as the effective heterogeneous nucleus of α-Al [19]. However, when Al_3Ti particles appear, i.e., using Al-5Ti-B as a refiner of aluminum alloy, TiB_2 particles interact with Al_3Ti particles to refine aluminum alloy, and the Ti from Al_3Ti phase spontaneously enriches on the surface of TiB_2 particles. This can provide a sufficiently high interface chemical potential to make the interface energy between the TiB_2 particles and the surrounding liquid phase drop below the liquid-solid interface energy of Al, thus stimulating the nucleation potential of TiB_2 particles and causing α-Al to produce an effective heterogeneous nucleus [18]. In the preparation of Al-5Ti-B by fluoride salt reaction, the aggregation of TiB_2 phase occurs, which would reduce the refining effect of Al-5Ti-B. However, after adding Gd, the aggregation of TiB_2 phase was not found under transmission electron microscope. This may be due to the enrichment of rare earth elements at the front edge of the phase interface during the solidification of α-Al, which promotes the dispersion of TiB_2 phase.

4 Conclusions

The effects of the introduction of rare earth element Gd on microstructure and refinement performance of Al-Ti-B alloy on aluminum alloy were investigated. The following conclusions can be obtained:

(1) In the Al-5Ti-B refiner prepared by conventional fluorine salt method, there is a thick Al_3Ti phase on the matrix. After adding 1.0wt.% Gd, Al_3Ti phase is refined, which improves the refining performance of Al-5Ti-B alloy.

(2) When 1.0wt.% Gd is added to the Al-5Ti-B alloy refiner, $Ti_2Al_{20}Gd$ phase appears at the edge of part of Al_3Ti phase, and there is no compound layer at the interface between $Ti_2Al_{20}Gd$ phase and aluminum matrix, and the lattice mismatch degree between $Ti_2Al_{20}Gd$ phase and aluminum matrix is quite great, so $Ti_2Al_{20}Gd$ phase cannot be used as heterogeneous nuclei of α-Al. However, when $Ti_2Al_{20}Gd$ phase is decomposed into Al_3Ti phase and Gd element in aluminum melt, the refining performance of the refiner can be significantly improved.

(3) There are a great number of TiB_2 particles smaller than 1 μm dispersedly distributed in the Al-5Ti-B-Gd refiner. These particles can become effective heterogeneous nuclei and promote the refinement effect of the refiner.

References

[1] Xu X X, Feng Y T, Fan H, et al. The grain refinement of 1070 alloy by different Al-Ti-B mater alloys and its influence on the electrical conductivity. Results in Physics, 2019, 14(9): 1024–1030.

[2] Matveev A, Zhukov I, Ziatdinov M, et al. Planetary milling and self-propagating high-temperature synthesis of Al-TiB_2 composites. Materials, 2020, 13(5): 1050–1058.

[3] Jia Y W, Huang H J, Fu Y N, et al. An in-situ investigation of the solute suppressed nucleation zone in an Al-15wt.% Cu alloy Inoculated by Al-Ti-B. Scripta Materialia, 2019, 167: 6–10.

[4] Ding W W, Zhao X Y, Chen T L, et al. Effect of rare earth Y and Al-Ti-B master alloy on the microstructure and mechanical properties of 6063 aluminum alloy. Journal of Alloys and Compounds, 2020, 830(25): 154–160.

[5] Wang X J, Xu C, Muhammad A, et al. Effects of Al-Ti-B-RE grain refiner on microstructure and mechanical properties of Al-7.0Si-0.55Mg alloy. Transactions of Nonferrous Metals Society of China, 2014, 24(7): 2244–2250.

[6] Wang Z J, Si N C. Effect of the morphology and distribution of the second phases of Al-Ti-B-RE master alloys on refining commercially pure aluminum. Rare Metal Materials and Engineering, 2015, 44(6): 1494–1499. (In Chinese)

[7] Ma T F, Chen Z Y, Nie Z R, et al. Microstructure of Al-Ti-B-Er refiner and its grain refining performance. Journal of Rare Earths, 2013, 31(6): 622–670.

[8] Yin D S, Zhao J T, Zhang Z K. Effect of Mg-30% Gd on dimensions distribution of $TiAl_3$ particles in Al-5Ti alloys. Foundry Equipment and Technology, 2015 (4): 22–24. (In Chinese)

[9] Birol Y. Production of Al-Ti-B master alloys from Ti sponge and KBF_4. Journal of Alloys and Compounds, 2007, 440(1–2): 108–112.

[10] Yang M S, Wang Z F. Investigation of intermetallic compound formed from rapid solidification of Al-Ti-RE alloy. Journal of Rare Earths, 2004, 22(2): 311–314.

[11] Jia Y W, Wang S C, Shu D. Grain size prediction and investigation of 7055 aluminum alloy inoculated by Al-5Ti-1B master alloy. Journal of Alloys and Compounds, 2020, 821: 153504.

[12] Nie J F, Liu X F, Ma X G. Influence of trace boron on the morphology of titanium carbide in an Al-Ti-C-B master alloy. Journal of Alloys and Compounds, 2010, 491(1–2): 113–117.

[13] Li P T, Li Y G, Nie J F, et al. Influence of forming process on three-dimensional morphology of TiB_2 particles in Al-Ti-B alloys. Transactions of Nonferrous Metals Society of China, 2012, 22(3): 564–570.

[14] Huang Y C, Shao H B, Xiao Z B, et al. First principle study of AlB_2, TiB_2 and $TiAl_3$ in Al-Ti-B alloy. The Chinese Journal of Nonferrous Metals, 2018, 28(8): 1491–1498. (In Chinese)

[15] Jia Y W, Wang S B, Huang H J, et al. In situ observation of the Zr poisoning effect in Al alloys inoculated by Al-Ti-B. Metallurgical and Materials Transactions A, 2018, 49(21): 4771–4784.

[16] Julius C. Schuster Martin Palm. Reassessment of the binary aluminum-titanium phase diagram. Journal Phase Equilibria and Diffusion, 2006, 27(3): 252–256.

[17] Wei W, Mao R Y, Wei K X, et al. Effect of equal channel angular pressing on microstructure and grain refining performance of Al-5%Ti master alloy. Materials Science & Engineering A, 2013 564: 92–96.

[18] Wang Z J, Si N C. Synthesis and refinement performance of the novel Al-Ti-B-RE master alloy grain refiner. Rare Metal Materials and Engineering, 2015, 44(12): 2970–2975.

[19] Zhang L L, Jiang H X, Zhao J Z, et al. A new understanding toward effect of solute Ti on grain refinement of aluminum by Al-Ti-B master alloy: Kinetic behaviors of TiB_2 particles and effect of solute Ti. Acta Metallurgica Sinica, 2017, 53(9): 1090–1098. (In Chinese)