Precipitation of TiAl₃ in remelting Al-5Ti-1B and the grain refinement of 7050 alloy

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Keywords: Al-5Ti-1B alloy, grain refinement, TiAl₃ compound, mechanical properties

Abstract
This paper studies the precipitation regularity of TiAl₃ compound in different temperature, holding time and cooling rate. Besides, this paper studies the influence of Al-5Ti-1B on the mechanical properties of the 7050 alloy such as the aluminum alloy grain size, microstructure and strength through changing holding time and amount of Al-5Ti-1B. Through water cooling, the solute Ti forms new fine TiAl₃ compounds firstly. While through natural cooling, the solute Ti is easy to grow up around the agglomerate TiAl₃ compounds. The variation of the undissolved TiAl₃ compound as follows: the size of the block-like TiAl₃ does not change at 700 °C for 10 min; while the size has stabilized at 750 °C for 5 min. The dissolution of the rod-like TiAl₃ is not obvious when holding for 20 min, but the rod-like TiAl₃ fuses easily. After adding the Al-5Ti-1B into the 7050 alloy, the grain shape of α-Al changes from dendritic crystal to equiaxed crystal, and the refining effect is obvious; While the adding amount increases, the size of α-Al become larger, but it has a tendency towards to dendritic crystal. The mechanical properties of 7050 alloy without Al-5Ti-1B is in the worst condition. Transcrystalline rupture may occur in grain of 7050 alloy in tensile test due to it is coarse grain. After adding the refiner, the mechanical properties are optimal when keeping the temperature 750 °C for 5 min. Dimple could be found in the tensile fracture, and the dimples mainly are equiaxial.

1. Introduction

Aluminum alloy has low density, high strength, high elastic modulus and good corrosion resistance. It has become the most potential new structural material in automobile, military and aerospace industries. With the wide application of aluminum alloy in aerospace, it is required to have excellent mechanical properties and good processing performance. Grain refinement can not only change the microstructure into fine equiaxed grains, but also improve the strength, plasticity and toughness of aluminum alloy [1–4]. In addition, the refinement of aluminum alloy can make the structure compact and reduce segregation, which is convenient for the subsequent plastic deformation of ingot [5].

It is widely accepted that transition metal elements such as Zr, Ti, V, Sc and nonmetal elements B, C exhibit excellent refining performance on α-Al grains [6–9]. Cibula proposed ‘carbide boride theory’ and further studied grain refiners containing Ti and B [10–12]. Ti powder, KBF₄ and buffer were mixed and pressed into Ti-B tablet to add aluminum melt in use. However, the melt was easily polluted in processing engineering. Subsequently, Al-Ti alloy ingot and more effective Al-Ti-B master alloy ingot appeared in the field of aluminum grain refiner.

Al-5Ti-1B master alloy is widely used in Al-Ti-B master alloy. It is an excellent alloy for grain refinement of aluminum and aluminum alloy [13–15]. The addition of Al-5Ti-1B master alloy into the aluminum melt will release TiAl₃, TiB₂, AlB₂, or (Al,Ti)B₂ intermetallic phases. The size, shape and distribution of TiB₂ particles and TiAl₃ phase determine the final grain refinement effect of master alloy to a great extent. The fine size, uniform distribution of TiAl₃ and dispersed distribution of TiB₂ particles are the outstanding characteristics of Al-5Ti-1B master alloy. Jones and Pearson used Ti and B as master alloy ingots to add aluminum melt [16]. Compared with
salt solvent method, it can not only improve the cleanliness of the melt, but also have better grain refinement effect. However, after the Al-Ti-B master alloy ingot is added into the furnace, there are still problems of coarse compound and composition segregation. Y.F. Han prepared Al-5Ti-1B master alloy by applying high-energy ultrasound in the process of fluoride salt reaction, which improved the morphology and distribution of TiB₂ and TiAl₃ phases in the structure, and more importantly, greatly reduced the average size and size distribution span of TiB₂ particles [17, 18]. Adding rare earth elements to Al-Ti-B system can significantly improve the morphology and distribution of TiAl₃ and TiB₂ phases in the structure, and it is considered that it is more efficient and long-term than Al-Ti-B refiner [19, 20]. However, there is still a lack of in-depth study on its refining mechanism and refining stability. Compared with Al-Ti-B system, rare earth elements are surface active materials, which are easy to adsorb and segregate on the grain boundary and phase interface of aluminum, and fill the defects on the interface, thus hindering the growth of TiAl₃ and TiB₂, and refining the size of TiAl₃ and TiB₂ particles. Rare earth elements are very easy to form AlTi rare earth compound with Al and Ti, and dissolve into the aluminum melt quickly, which reduces the surface energy, increases the wettability of aluminum melt to boride and aluminide, and makes TiB₂ difficult to agglomerate, so as to inhibit the decline and improve the refining effect [21–23]. Rare earth is also easy to accumulate in the front of crystallization, resulting in undercooling of aluminum melt composition, hindering the growth of α-Al grains, and promoting the further nucleation of α-Al on the refined core [24, 25].

At present, most of the research on this aspect mainly focuses on the special treatment methods, but the research on the dissolution and precipitation of TiAl₃, second phase in Al-5Ti-1B master alloy during remelting process and the precipitation rule of TiAl₃ compound by remelting parameters are not clear enough.

In this study, the precipitation of TiAl₃ in Al-5Ti-1B master alloy was studied by water quenching and natural cooling at low temperature and different holding time. The changes of size and morphology of TiAl₃ under different conditions were studied. Al-5Ti-1B master alloy with 0.6 wt% was added to 7050 alloy and kept at 750 °C for different time; Adding 4 wt% Al-5Ti-1B master alloy into 7050 alloy, and holding at 750 °C for 5 min. The 7050 alloy melt with and without grain refiner was partially poured into Reynolds standard golf T-mold to observe the grain size and microstructure of the alloy; The other part was

### 2. Materials and methods

#### 2.1. Material preparation

The nominal chemical composition of 7050 alloy used in this work is Al-6.4Zn-2.3Mg-2Cu-0.12Zr-0.1Mn (all compositions are in wt% unless otherwise stated) and its actual chemical composition detected by an Inductively Coupled Plasma-Atomic Emission Spectrometer PE8000 machine (SPECTRO, Germany) is shown in table 1. Commercial purity Al (99.7%), Zn (99.9%), Mg (99.9%), Cu (99.9%), sponge Ti (99.5%) and electrolytic Mn (99.5%) were used as raw materials to prepare 7050 alloy. Firstly, the weighted metals were melted in a clay crucible by using an intermediate frequency furnace. Secondly, the melt was transferred to a resistance furnace to keep melting temperature stable.

The Al-Ti-B master alloy (provided by Shandong Al & Mg Melt Technology Co. Ltd.) has a nominal chemical composition of Al-5Ti-1B. The chemical compositions of the Al-5Ti-1B shown in table 2.

| Table 1. Actual chemical compositions of 7050 alloy detected by spectrum. |
|-----------------|------------|-------------|--------|--------|--------|--------|--------|
| Alloy  | Zn (wt%)  | Mg (wt%)  | Cu (wt%)  | Zr (wt%) | Mn (wt%) | Si (wt%) | Fe (wt%) | Al (wt%) |
| 7050   | 6.84      | 2.29       | 2.30     | 0.119   | 0.0883  | 0.0479  | 0.078   | Bal.     |

| Table 2. Chemical composition of Al-5Ti-1B master alloy. |
|-----------------|------------|-------------|--------|
| Alloy  | Ti (wt%) | B (wt%) | Fe (wt%) | Si (wt%) | V (wt%) | Al (wt%) |
| Al-5Ti-1B      | 4.5 ~ 5.5 | 0.8 ~ 1.2 | <0.2    | <0.35   | <0.35   | Bal.     |
poured into the cast iron mold, and the non-standard tensile samples were processed, and the tensile test was carried out, and the fracture morphology was observed.

The microstructure analysis of Al-5Ti-1B and 7050 alloys was conducted using SU-70 field emission scanning electron microscope (FESEM) equipped with EDX detector.

3. Results and discussions

3.1. Precipitation of TiAl3 at different cooling rates

Figure 1 shows the microstructure of massive TiAl3 compound at 700 °C for 5, 10, and 20 min under water cooling condition. The size of the block TiAl3 compound was about 60 μm when it was kept at 700 °C for 5 min with the increase of holding time, the size of the block TiAl3 compound decreased to about 50 μm after holding for 10 min, and some smaller TiAl3 compounds began to exist. It can be observed that there are a small amount of regular massive TiAl3 compound and some fine TiAl3 particles at the interface of aluminum melt, as shown in figure 1(b); When the reaction time reaches 20 min, the size of the compound remains about 40–50 μm, which is no longer significantly reduced, but there will be a small number of TiAl3 particles with round interface and about 10 μm size, as shown in figure 1(c).

Compared with the size change of massive TiAl3 compound after 700 °C remelting of Al-5Ti-1B master alloy, the size change of bar TiAl3 compound with larger long axis size is not obvious. As shown in figure 2, when the holding time reaches 5 min, the long axis dimension of bar like TiAl3 compound is 70–80 μm, which has no obvious change compared with that of bar like TiAl3 compound in unfused master alloy, after holding for 10 min, most of the sizes are still about 70 μm. However, it is found that a small amount of bar like TiAl3 compounds fuse in the middle part, so the bar like TiAl3 compounds with smaller long axis size can be obtained.

The stability of the block TiAl3 at 700 °C is poor, and it can be dissolved in a short time, and it is easy to get small TiAl3 particles from the large block splitting. On the contrary, the rod TiAl3 compound is relatively stable, with almost no change in morphology and size. Only a small number of rod TiAl3 compounds fuse, resulting in shorter rod TiAl3 compounds.
3.2. Precipitation of TiAl3 under natural cooling

In this study, natural cooling refers to the air-cooled casting of cast iron mold, the cooling rate is relatively slow, and the solute Ti in the remelted Al-5Ti-1B master alloy will be fully diffused when the TiAl3 compound is re-precipitated.

Figure 3 shows the microstructure of Al-5Ti-1B master alloy after holding at 750 °C for 5, 10 and 20 min respectively. It can be seen from the figure that with the prolongation of holding time, TiAl3 compounds have different degrees of agglomeration, and the particle size is also changing. Figure 3(a) TiAl3 compounds with different morphologies and sizes can be observed to gather together. Figure 3(b) The precipitation of solute Ti can be observed between TiAl3 compounds agglomerated in the matrix. Figure 3(c) TiAl3 compound with the size of 200 μm appeared in the crystal, and it was observed that TiAl3 was formed by multiple TiAl3 conglutination and growth.

It can be seen from figure 3(a) that TiAl3 compound agglomeration occurs in Al-5Ti-1B master alloy with holding time of 5 min. When the holding time is further extended, the agglomeration of TiAl3 compounds becomes more and more serious. When the holding time reaches 20 min, a large number of TiAl3 compounds are aggregated to form adhesive compound groups. These conglutinated compounds form concave surfaces, where a large amount of solute Ti preferentially nucleates and grows up. Finally, these agglomerated TiAl3 will grow into new TiAl3 compounds with super large size.

Comparing the size of TiAl3 compound in figures 3(a), (b) and (c), it can be found that holding for 5 min and 20 min does not further reduce the size of TiAl3 compound, which indicates that the dissolution process of TiAl3 compound in high temperature aluminum melt has ended when holding for nearly 5 min, which is consistent with the size change rule of TiAl3 compound at 750 °C for different holding time under water cooling condition. This phenomenon will result in the large size of TiAl3 compound in the remelted Al-5Ti-1B master alloy, which is difficult to dissolve into the aluminum melt when it is added into the aluminum alloy to be refined, thus reducing the refining effect of the master alloy. At 700 °C, the amount of TiAl3 compound dissolved is less, so there are a lot of regular angular TiAl3 compounds, and the solute Ti dissolved into the aluminum melt is also less. With the prolongation of holding time, although the agglomeration and adhesion of TiAl3 compound
appeared, due to less solute Ti in the aluminum melt, the agglomeration compound did not appear and grew into a new TiAl₃ compound with super large size.

### 3.3. Microstructure and mechanical properties of 7050 alloy refined by Al-5Ti-1B

As shown in Figure 4, compared with samples 1, 2 and 3, the grain size increases slightly with the prolongation of holding time. This is because TiB₂ particles with the size of about 1 μm are easy to agglomerate in the aluminum melt, and are easily pushed to the grain boundary by α-Al grain boundary. When the holding time is further extended, a large number of agglomerated TiB₂ particles will further increase the size of TiAl₃ compound, which will reduce the refining effect and increase the grain size of α-Al.

The results show that the grain size of sample 4 is larger than that of sample 1, and the equiaxed grains tend to grow into dendrites. This is because in the aluminum melt, when the amount of Al-5Ti-1B master alloy is high, TiB₂ particles in 7050 alloy begin to agglomerate, and large-size TiAl₃ compound will precipitate during solidification, and further agglomerate and grow up, thus reducing the refining effect [26]. Because of the easy formation of large TiAl₃ compounds, the number of TiAl₃ is reduced, that is, the effective nucleation core is reduced. From the kinetic point of view, the large TiAl₃ and TiB₂ particles are easy to precipitate, resulting in the failure of refining and nucleation. When the addition of Al-5Ti-1B master alloy is large, TiAl₃ and TiB₂ are easy to agglomerate and precipitate to the bottom, and can not play the role of heterogeneous nucleation.

Adding Al-5Ti-1B master alloy to 7050 alloy can refine the grain size. Grain refinement not only has the effect of fine grain strengthening, but also can improve the plasticity of the alloy.

Figure 5 shows the mechanical properties of different samples of 7050 alloy after adding Al-5Ti-1B master alloy. After adding the refiner, the mechanical properties of the system were the best when the holding time was 5 min. With the increase of the heat preservation time, the mechanical properties decreased. Compared with samples 1 and 4, the mechanical properties of 7050 alloy decrease when more refiner is added. The test results of mechanical properties show that the decrease of grain size can improve the strength and elongation of 7050 alloy.

Figure 6(a) shows the fracture morphology of 7050 alloy without Al-5Ti-1B master alloy. The microstructure of 7050 alloy is dendritic grain with coarse size. The number of grains per unit volume is small, and the area of grain boundary is also small. Therefore, when the alloy is subjected to tensile stress, the
dislocation source inside the grain begins to produce dislocations, and the grain boundary obstruction is small, that is, the tensile strength and other mechanical properties are low. Due to the coarse grain size of the alloy, the grain is prone to transgranular fracture when it is stretched to a certain stress, as shown in figure 6(a). The crack indicated by the arrow in the figure is transgranular fracture.

It can be seen from figures 6(b) and (c) that the 7050 alloy with refiner will produce more dimples during tensile fracture, mainly equiaxed dimples. Samples 1 and 4 are added with different amounts of Al-5Ti-1B master alloy respectively, so as to obtain more and smaller equiaxed grains. Therefore, the larger the grain boundary area per unit volume, the greater the stress of dislocation source in the adjacent grain, that is, the greater the deformation can be achieved before the 7050 alloy breaks, and the good mechanical properties are shown.

4. Conclusions

(1) The microstructure of Al-5Ti-1B master alloy remelted and quenched by water shows that the size of massive TiAl$_3$ does not change when it is kept at 700 °C for 10 min, but it is stable when it is kept at 750 °C for 5 min. The dissolution of TiAl$_3$ was not obvious within 20 min, but the phenomenon of fusing occurred.
(2) The microstructure of remelting Al-5Ti-1B alloy under natural cooling and holding temperature of 750 °C for 5, 10 and 20 min showed that with the prolongation of the holding time, the TiAl₃ compounds agglomerated in different degrees, and a large number of new TiAl₃ compounds were formed by the adhesion of several TiAl₃ compounds.

(3) After adding Al-5Ti-1B master alloy into 7050 alloy, the α-Al grain changes from dendrite to equiaxed grain, and the refining effect is obvious. When the addition amount is 0.6 wt%, the change of holding time has little effect on the refining effect. When the content of α-Al is increased to 4.0 wt%, the grain size of α-Al increases, but it is still equiaxed and tends to be dendrite.
(4) The results show that the mechanical properties of 7050 alloy without Al-5Ti-1B master alloy are the worst, and transgranular fracture is easy to occur during tensile fracture due to coarse grains; after adding refiner, the mechanical properties of 7050 alloy with holding time of 5 min at 750 °C are the best, and more dimples, mainly equiaxed dimples, will appear during tensile fracture.

Acknowledgments

This research has been supported by the Aviation Foundation of China.

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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