Microstructure and Mechanical Properties of Purity Aluminum Refined with Salt Containing Ti and B Elements*

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The microstructure and mechanical properties of purity aluminum refined with salt containing Ti and B elements have been studied in detail with Optical Microscope and MTS (Mechanical Testing and Simulation). The salt containing weight ratio of 22.2 Ti : 1 B has the most refining effect on the purity aluminum with the finest structure and the best mechanical properties, meanwhile it also possesses the advantages of short reacting time (within 5 minutes) and long fading time (more than 20 hours). The refining effect of the salt increases with the content of Ti and B in the melting and the refining mechanism is mainly contributed to the heterogeneous nuclei of more fine TiAl3 particles dispersed in the melting, which come from the reaction between the salt and aluminum. Purity B contained salt has little or no directly refining effect, However, B contained salt has indirect refining effect on the purity aluminum when it is added simultaneously with Ti contained salt, this may be due to that the dispersive and fine boride (TiB2) could be taken as the heterogeneous nuclei for TiAl3 particle, and then prevents the coarsening of the TiAl3 particle.

Key Words: Purity Aluminum, Structure and Mechanical Properties, Heterogeneous Nuclei, Refining Mechanism

1. Introduction

Mechanical property of purity aluminum can be improved by alloying or refining method, especially by the chemical refining. Chemical refining is sometime more convenient and necessary. The conventional refiners are mainly the master alloy of Al-B, Al-Ti, Al-Ti-B, and Al-Ti-C etc.(1)-(9) In addition, Al-Ti-C-Re and Al-Ti-B-Re are also reported(10)-(13). However they still have their own deficiencies. It needs to design addition processes to achieve the most effective grain refinement. Such as, qualification master alloys must be prepared firstly, and sometimes, the master alloys had better to be changed into smaller size or powder by deformations to obtain more effective refinement(3),(4),(6),(7). Finding the contact time with the finest grain refinement (critical contact time) is another problem. If the contact time is much too short, the finest grain size may not be achieved. On the contrary, if the contact time is much too long, the grain refiner will be faded(14). Meanwhile, the essential refining mechanism and fading mechanism are still unclear or inconsistent(1)-(9),(14),(15).

If salt refiner containing Ti and B elements was directly used to refine the aluminum, it can save much time and cost, comparing with the addition of the master alloy contained same elements. However, there are a few papers concentrated on this field and exist many problems to be solved, such as contacting and fading time, refining and fading mechanism etc.(16),(17) In this study, the effect of salt containing Ti and B elements on the purity aluminum was studied in detail. Meanwhile the refining mechanism was also investigated by SEM-EDAX and thermodynamics calculation.

2. Experimental Procedure

Commercially pure aluminum with more than 99.9 wt% Al was served as experimental material, and commercially pure K2TiF6 salt, KBF4 salt and mixtures of K2TiF6 and KBF4 with various weight ratio of Ti/B (salt mixtures) were served as refiners. The particle size of salts is about 75 µm and the purity is more than 99.0 wt%.

Purity aluminum was molten in Al2O3 crucible with resistant furnace to 750°C. Salt mixtures with different ratio of Ti/B and different contents were added to the molten aluminum. After manual stirring, removing slag and different holding time, the molten aluminum was cast into
iron mould, and it was preheated to 200°C before casting(16),(17).

Samples were cut along transversal section and 20 mm apart from the ingot bottom, then grounded and polished. Macrostructure were etched in acids mixture of 5 mL HF-40%, 75 mL HCl-38%, and 25 mL HNO₃-68% and recorded with digital camera. Microstructure were etched in 4%HF solution and recorded with Nikon-L150 Optical Microscope. Mechanical properties of the samples were measured by MTS and three measured values were averaged as results. Optical Microscope and JSM-6700F scanning electron microscope with EDAX were used to observe the size and constitution of the heterogeneous nuclei in α-Al grain. Thermodynamic calculation and analysis were used to investigate the refining mechanism.

3. Results and Discussion

3.1 Effect of Ti/B ratio on the macrostructure and properties

Figure 1 shows the typical macrostructure of the purity aluminum refined by salt mixtures with different ratios of Ti/B, which was held 30 minutes after added to the melting. The relative mechanical properties measured with MTS are shown in Fig. 2.

It is clear from Fig. 1 that the macrostructure of ingots without refiner accords to the morphology of typical castings with a thinning-layer in fine grain, then columnar grain and coarsening equiaxed grain from surface to center in turn. However, the effect of the salts with different ratio of Ti/B on the macrostructure of purity aluminum changed markedly. The refining degree from maximum to minimum was successively salt mixtures with the weight ratio of Ti/B 22.2/1, 13.3/1, 5.3/1, 2.3/1 or purity Ti contained salt and purity B contained salt, while the purity B contained salt has little or no directly refining effect. This indicates that Ti contained salt, especially the Ti and B contained mixed salts is more effective refiner for the purity aluminum.

The changing trend of mechanical properties in the Fig. 2 is similar to the macrostructures. It reconfirms that the salt with the ratio of Ti/B 22.2/1 is most effective.

3.2 Effect of the content of Ti and B on the macrostructure and properties

Different contents of salt with fixed ratio of 22.2 Ti/1B were added to the molten purity aluminum, and then cast it into mould after stirring, removing slag and holding 30 minutes. Figure 3 shows the evolution of typical macrostructure.

It is clear by comparing Fig. 3 (a) – (d) that the refining degree of the salts first increases markedly with the increase of the Ti addition from 0 to 0.10 wt%, then slowly from 0.10 to 2.0 wt%Ti. This means that the refining effect of the salt has a saturated addition with approximate 0.10 – 0.2 wt% Ti, it can be ascertained from the saturation of mechanical properties in Fig. 4. A similar saturation phenomenon was observed with the addition of Al–3 wt% Ti–2 wt% B master alloy(4).
mould after stirring, removing slag and holding different time. Typical macrostructure and microstructure of the samples are shown in Figs. 5 and 6, respectively.

It is found by comparing the results in Figs. 5 and 6 that both the macrostructure and microstructure of the cast can be refined markedly and quickly within 5 minutes after adding salt refiner, and it still remains fine even though holding time extends to 20 hours. Using the Al-Ti-B master alloy as the refiner for the purity aluminum, however, not only the fading time was less than 120 minutes, but also it needs longer time to reach effective refining (3). This implies that the salt refiner containing Ti and B elements possesses advantages of quicker effecting time and longer fading time comparing to the master alloys.

3.4 Discussion of refining mechanism

3.4.1 Thermodynamic analysis

Following reactions (1) – (3) can be occurred when the salt containing Ti and B elements were added into aluminum melting.

\[ Ti + 3Al = TiAl_3 \]  
\[ Ti + 2B = TiB_2 \]  
\[ Al + 2B = AlB_2 \]  

Take 0.2 wt%Ti and 0.009 wt%B as the content of Ti and B in the melting, then the change in Gibbs energy (\( \Delta G \)) of the reactions (1) – (2) calculated according to the Zhang (17) are \(-79622 J\) and \(-125839 J\), respectively, while the \( \Delta G \) in reactions (3) is \(70791 J\). This means the reactions (1) – (2) can be progressed spontaneously from left to right below \(1023 K\), while the reaction (3) progresses in negative direction. That is to say, the resultants of TiAl3 and TiB2 or (Ti, Al)B2 are stable, while the AlB2 is unstable in melting below the temperature of \(1023 K\).

That is why the purity B contained salt has little or no directly refining effect as non-existing of AlB2 in the melting, however, the B contained salt has indirectly refining effect on the purity aluminum when it is added simultaneously with Ti contained salt as existing of TiB2 or (Ti, Al)B2 in the melting (see Figs. 1 and 2). This may be due to that the dispersive and fine boride in the melting could be taken as the heterogeneous nuclei for TiAl3 particle, and then prevents the coarsening of the TiAl3 particle (15) (17). It is shown that the smaller the size of TiAl3 particle, the smaller the averaged size of \(\alpha\)-Al grain, that is to say, the more refining effect (17).

Melting temperature and holding time are major factors determining the size of TiAl3 particle, while the size of salt powder and the cooling rate are minor determining factors.

3.4.2 Microstructure of heterogeneous nuclei

The site, size and morphology of the heterogeneous nuclei in the purity aluminum refined with salt containing 2.0 wt%Ti+0.09 wt%B were shown in Fig. 7. The constitution of central particle and matrix measured by SEM-EDAX are listed in Table 1.

It is obvious from Table 1 that the central particles
in the α-Al grain are TiAl3. So it can infer that the α-Al grain nucleates and grows around the heterogeneous nuclei–TiAl3. Further investigation on the morphology, site and constitution of the heterogeneous nuclei of TiB2 and the role of B element in the refining purity aluminum by EPMA will be published in other paper.

We can further find from Fig. 7 that the most α-Al grain entraps one or more rounder TiAl3 nuclei with the averaged size about 5 μm, while the averaged size of α-Al grain is about 60 μm.

3.4.3 Density of TiAl3 nuclei in the molten aluminum

A large number of high melting point TiAl3 nuclei (> 660°C) will formed in the melting when Ti contained salt was added into the molten purity aluminum. During solidification, α-Al phase will nucleate around the heterogeneous nuclei, meanwhile, these fine TiAl3 particles themselves coarse, too. So the size and the density of TiAl3 particle plays an important role in refining the castings of purity aluminum. In the following, the number density of TiAl3 in the molten aluminum is estimated. Let the densities of TiAl3 and Al are 3.360 kg/m³ and 2.700 kg/m³, respectively, and the Ti content added to the molten aluminum with salt is 0.2 wt%. It is known from calculation with reaction (2), the equilibrium content of Ti in the molten aluminum at 1023 K (ΔG_{1023} = 0) is about 1.2 x 10⁻⁴ wt%, which means that almost all the added Ti to the molten will react into TiAl3.

Taking TiAl3 and α-Al are sphere with averaged diameter of ~ 5 μm and ~ 60 μm, respectively, according to Fig. 7. Then the calculated number density of heterogeneous nuclei TiAl3 per α-Al grain is approx 7.5. It is obviously that lots of TiAl3 in the molten will markedly refine aluminum castings. In reality, many excess TiAl3 particles will coarsen and congregate along α-Al grain boundary such as in the Fig. 7.

4. Conclusions

(1) The refining effect of Ti and B contained salt on the purity aluminum varies markedly with the ratio of Ti/B and the best ratio is 22.2 Ti/B. Meanwhile, the refining effect improves with the increase of Ti and B content in the melting.

(2) The salt containing Ti and B, especially with the ratio of 22.2 Ti/B, is the best choice refiner. It not only can markedly refine the α-Al grain, but also play a refining role within short time and has a long fading time.

(3) The refining mechanism of Ti and B contained salt on the purity aluminum is mainly due to the nucleation of α-Al grain around the heterogeneous nuclei–TiAl3, while (Al,Ti)B2 has little or no refining effect, but B element has indirect refining effect on the purity aluminum when it is added simultaneously with Ti atom.

References


