The critical effect of Fe on the grain refinement of aluminium via Al-5Ti-1B addition

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Abstract. The influence of Fe on the nucleation potency of TiB_2 particles was investigated by employing grain refinement of high purity aluminium in this study. Experiment results showed that without Fe, high purity aluminium cannot be refined by 0.8wt.% addition of Al-5Ti-1B. However, high purity aluminium containing 0.08wt.% Fe can be refined effectively by 0.2wt.% addition of Al-5Ti-1B, its grain size was about 206μm in diameter. Fine equiaxed grains of about 153μm in diameter can be obtained for high purity aluminium containing 0.08wt.% Fe and 0.006wt.% Ti. Grain refinement mechanism should include nucleation and dendrite remelting and multiplication. Both nucleation and dendrite remelting and multiplication played essential role on the grain refinement of aluminium. The effect of Fe was linked to increase active nuclei by segregation on TiB_2 surface and then to promote nucleation of α-Al. The performance of Ti was to enhance the dendrite remelting and multiplication by forming small conglomeration zones of Ti atoms concentrated around TiB_2 particles.

1. Introduction

Addition of Al-Ti-B mater alloys into molten aluminium has become a standard and effective practice in aluminium foundries worldwide in order to enhance mechanical properties, reduce ingot cracking, improve feeding, improve the homogeneity of the cast structure by obtaining fine, equiaxed grains after solidification. To understand the mechanism of grain refinement and to promote the development of Al-Ti-B refiner, during the last several decades, various theories had been proposed to explain the experimental observations. There is a friendly consensus that the excess Ti and TiB_2 particles are necessary and important for commercial pure aluminium (CPAl) obtaining a good grain refinement result [1-7].

Ti was considered as the strongest element to act as growth restriction factor (GRF). Usually, Q is referred to as the growth restriction factor, and is a measure of the growth-restricting effect of solute elements on the growth of the solid-liquid interface in the absence of solute interactions [3, 8, 9]. It is defined as $mc_0(k-1)$, where m is the slope of the liquidus, C_0 is the concentration of the solute in the alloy, and k is the equilibrium partition coefficient between the solid and liquid at the growing interface. Empirically, the average grain size can be described as a liner function of 1/Q for various Al alloy. The effects of solute content on grain refinement in an isothermal melt studied by Men and Fan [10] indicate that 1/3 power law can describe the experimental data more accurately than a linear relationship.

For excess Ti, another important role is that it can change the interface between TiB_2 and Al by forming $TiAl_3$ interfacial layer. Shumacher and Greer [11-13] revealed that a thin $TiAl_3$ layer about

3nm in thickness was formed between the TiB_2 and the α-Al by observation of $Al_{85}Y_8Ni_5Co_2$ metal glass inoculated with an Al-Ti-B master alloy. Mohanty and Gruzleski [14] reported that the formation of interfacial $TiAl_3$ layer at the TiB_2/Al interface can nucleate α-Al, in which the interface was confirmed by electron probe micro-analytical techniques (EPMA) and the nucleation of α-Al was proved by observation of boride particle within equiaxed grains.

In principle, the mechanism of grain refinement is quite straight forward [14]. When the added Al-Ti-B master alloy dissolves, numerous potent heterogeneous nuclei (TiB_2 with $TiAl_3$ layer) are released and dispersed into the melt, and subsequently a large number of these sites act as active nucleants during solidification [6, 14].

Our previous work testified that 0.2% addition of Al-5Ti-1B cannot refine high purity aluminium (HPAl) effectively [15, 16]. According to the dominant grain refinement mechanism, 0.2% addition of Al-5Ti-1B must refine HPAl effectively. But the experiment results against the prediction of dominant grain refinement mechanism. Therefore, we should reconsider the grain refinement mechanisms and try to explain the new phenomena reasonably. Furthermore, clearly the understanding of grain refinement mechanisms can promote further development of this kind of grain refiner.

For grain refinement, another very important method is to refine aluminium by physical method, including electromagnetic vibration [17-19], and pulse magneto-oscillation technique [20]. The principle of this kind of grain refinement mechanism is to achieve grain multiplication by promoting collapse of dendrite arms, dendrite fragmentation caused by vibration or stirring. Besides, another technique to achieve grain refinement using dendrite multiplication mechanism was made by Wannasin [21], in which gas bubbles were employed to agitate a molten metal during solidification. During this process, the "mother dendrites" created at the cold surfaces are fragmented resulting in grain multiplication. The physical method of grain refinement indicates that the dendrite remelting and multiplication plays an important role in the refinement process.

In the present study, to reveal the essence of grain refinement mechanism of aluminium properly, the effect of Fe, Si and Ti on the grain refinement of HPAl was investigated. According to the experiment results, an improved grain refinement mechanism was proposed.

2. Experiment
Al-5Ti-1B master alloys (LSM, UK) were employed for studying grain refinement of HPAl (>99.99wt.%Al, hereafter, all compositions are denoted in wt%). For studying the behaviour of Fe and Ti on the grain refinement process of HPAl, pure Fe and Al-10Ti were used for the present purpose. TP-1 testing method [22] was employed to evaluate the grain refinement performance of different refiner on aluminium. In each case the melt was maintained at 720±5ºC and slow stir was maintained to disperse refiner uniformity and keep the particles suspended in the melt for about 30 seconds with a graphite rod after addition was completed melting. The melt was held for 10 minutes and then cast into TP-1 mould. Each cone is sectioned perpendicular to its axis 38mm from its base for macro-analysis, ground mechanically on 200 grit and 400 grit water-proof adhesive papers and then etched in reagent (45 mL HCl, 15 mL HNO_3, 15 mL HF, 25 mL H_2O) to reveal the macro-structural feature. Normally, the sample for assessment of grain refinement was taken from the center of sample (center grain). For TP-1 sample, the solidification is occurred from the periphery of TP-1 mould to the center. Therefore, to assess the grain refinement properly, the periphery of TP-1 sample (periphery grain) was used to observe its microstructure evolution.

3. Results and discussion
Figure 1 is the grain structure of HPAl, HPAl refined by 0.2% addition of Al-5Ti-1B, and HPAl refined by 0.8% addition of Al-5Ti-1B, respectively. The average grain size is about 1000 μm, 500 μm and 350 μm for without refinement, 0.2% addition and 0.8% addition of refiner of HPAl. Compared to good refinement performance of Al-5Ti-1B refiner to CPAl, obviously, no effective refinement was obtained for HPAl even with 0.8% addition of refiner. In this case, very high excess Ti (0.0224wt% Ti for 0.8% addition of refiner) and a sufficient number of TiB_2 nuclei (four times to 0.2% addition of

refiner to HPAl) were added into the melt. The question is why there was no effective grain refinement was obtained, even though there were enough potent nucleation sites and very a high value of Q.
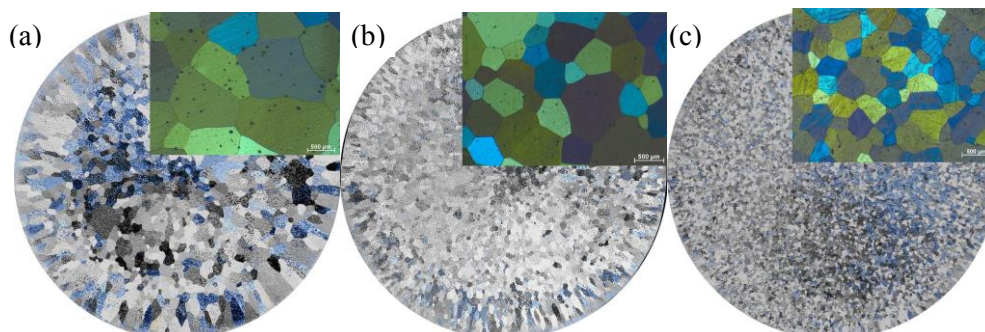

Figure 1. Grain structure of HPAl (inset is center grain structure), (a) without refinement, (b) refined by 0.2% Al-5Ti-1B, (c) refined by 0.8% Al-5Ti-1B.

It should be noticed that the big difference between CPAl and HPAl is that the CPAl contents 0.08% Fe, 0.03%Si and 0.006%Ti [15, 16]. The grain refinement of HPAl by 0.8% addition of refiner indicates that the value of Q caused by solute Ti does not play dominant role on grain refinement process, and excess Ti cannot make TiB_2 particles act as active nucleation sites. There should be another significant premise nucleation mechanism to make TiB_2 particles and solute Ti active.

According to the difference of composition between CPAl and HPAl, the impurities added into HPAl were 0.08% Fe and/or 0.06% Ti. It can be seen from figure 2 that the center grain size of HPAl containing 0.06% Ti refined by 0.2% addition of Al-5Ti-1B was about 450μm and was at the same level to HPAl refined by 0.2% addition of refiner. Also, very coarse column periphery grains were obtained. In this case, the excess Ti within melt was equal to CPAl refined by 0.2% addition of Al-5Ti-1B, its value is 0.0116%. If Q supplied by excess Ti plays important role on crystal growth, better grain refinement should be achieved. This demonstrates that the value of Q has very little effect on the grain refinement of aluminium. Figure 3 presents the grain size of HPAl containing 0.08% Fe refined by 0.2% addition of refiner. Fine equiaxed grains of about 206μm in diameter were obtained at the sample center (figure 3a). It should be noticed that fine column grains at the periphery of TP-1 sample were observed (figure 3b). Compared to the coarse column periphery grains of HPAl refined by 0.2% addition of Al-5Ti-1B (figure 1b), the change of periphery grain structure indicates that Fe can promote nucleation of TiB_2 particles with excess Ti.
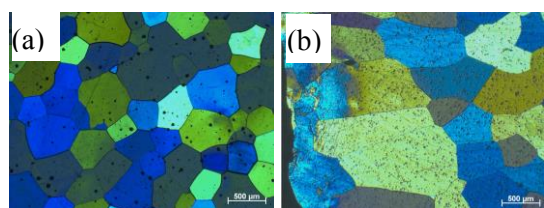

Figure 2. (a) Center grain and (b) periphery grain morphology of HPAl containing 0.006% Ti refined by 0.2% Al-5Ti-1B
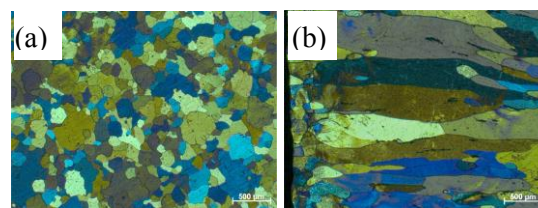

Figure 3. (a) Center grain and (b) periphery grain morphology of HPAl containing 0.08% Fe refined by 0.2% Al-5Ti-1B

The experiment results mentioned above show that Fe has strong influence on the grain structure of HPAl after refinement than that of Ti. These testified that Fe plays significant role on the grain refinement of aluminium.

The reciprocal effect of Ti and Fe on the grain refinement of HPAl was shown in figure 4. It can be seen that the periphery column structure disappeared completely (figure 4b) and there were very fine

equiaxed grains at the center of about 153μm in diameter (figure 4a). In view of the coarse grain structure for HPAl with 0.2% addition of Al-5Ti-1B, the better grain refinement results of HPAl containing Fe and Ti refined by 0.2% addition of refiner verify that the effect of excess Ti on the grain refinement is to enhance nucleation efficiency by dendrite melting and multiplication other than to promote nucleation potency of TiB_2 particles.
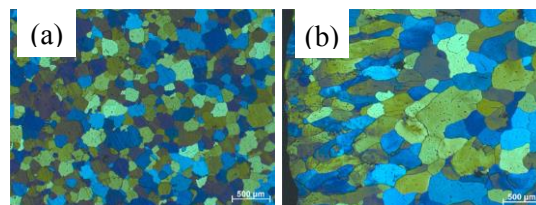

Figure 4. (a) Center grain and (b) periphery grain morphology of HPAl containing 0.08% Fe and 0.006% Ti refined by 0.2% Al-5Ti-1B.

Based on present experiment results, the grain refinement of aluminium should include nucleation, dendrite remelting and multiplication and solute Fe plays a significant role on the nucleation process. McKay's [23] observation on TiB_2/Al interface showed that Fe and Si were very easily segregated on TiB_2/Al interface. Combination present results and McKay's report, the conclusion of the promotion of the interface segregation on the potency of TiB_2 acted as active nucleation site can be drawn. This is why HPAl containing 0.08% Fe can be refined by 0.2% Al-5Ti-1B, while HPAl cannot be refined effectively. The periphery grain structure of HPAl containing 0.08% Fe after refinement was a convinced proof for our speculation (figure 3b).
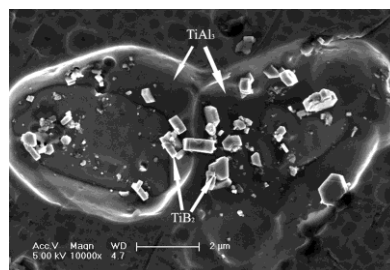

Figure 5. Microstructure of Al-5Ti-1B.

Careful investigation on the microstructure of Al-5Ti-1B grain refiner shows that TiB_2 particles were always found on the surface of $TiAl_3$ phase (figure 5). This was attributed to the good orientation relationship between TiB_2 and $TiAl_3$ [11-13]. Once solidification occurred, TiB_2 can act as the substrate of $TiAl_3$ phase. When refiner was added into melt aluminium, bulk $TiAl_3$ phase was melt quickly [2, 8]. But it does not distributed uniformly within melt due to the restriction effect of TiB_2. As a result, the Ti atoms were concentrated around TiB_2 particles to form many small conglomeration zones. During solidification process of refined aluminium, some of TiB_2 particles were act as active nuclei due to the segregation of Fe, and the other TiB_2 particles carried on Ti atoms zones to promote the dendrite remelting and multiplication. For HPAl refined by Al-5Ti-1B refiner, there are not enough active TiB_2 nuclei due to the absence of Fe segregation. This is why 0.2%, 0.8% addition of Al-5Ti-1B refiner cannot refine HPAl effectively while 0.2% addition of Al-5Ti-1B has good refinement performance on HPAl containing 0.08% Fe. For addition of TiB_2 and excess Ti into aluminium separately, the Ti atoms conglomeration zones (concentration fluctuations) are still exist within melt, but their size is much bigger than that of addition of Al-5Ti-1B, due to the absence of restriction of

TiB_2 particle. Then, there is indeed limited effect on the promotion of dendrite remelting and multiplication. With prolonging holding time or elevating holding temperature of refined aluminium melt, the small conglomeration zones of Ti will be decreased and disappear eventually. As a result, atoms of Ti tend to distribute uniformity within melt. This is the reason that the fading mechanism of grain refinement occurred at long-holding time and high temperature.

Compared to microstructure of refined HPAl with Fe and Ti, the effect of elements on the refinement process was revealed. Fe can promote the nucleation of TiB_2, and Ti can enhance refinement performance by the powerful ability of promoting fine dendrite remelting and multiplication. The different content of Ti on grain refinement performance of refined HPAl shows that there is a critical value for conglomeration zone of Ti atoms to promote the fine dendrite remelting.

Using this theory, poisoning effect of Zr, Mn and Cr on the Al-Ti-B refiner can be described reasonably. Normally, Zr, Mn and Cr were considered to form intermetallic compound and then to weaken the grain refinement by decreasing the Q value. In present study, the value of Q was testified that it was not the critical factor to refinement of aluminium. According to present experiment results, even with very high value of Q and plenty of TiB_2 particles, effective grain refinement did still not occur for HPAl. From this point of view, the essence of poisoning was attributed to insufficient active TiB_2 particles deduced by lack of Fe segregation, in which the formation of compound between Zr, Mn, Cr and Fe occurred. If more concentrate of Fe was added into melt, the grain refinement would be recovered. It was reported that the higher iron content can reduce the poisoning effect of zirconium [24]. This is well agreed with grain refinement mechanism proposed in present study.

4. Conclusion

In this investigation, the performance of Fe, Ti and TiB_2 on the grain refinement of aluminium was studied by employing Al-5Ti-1B refiner. According to the experiments results, Fe plays significant role on the grain refinement of aluminium and it can enhance nucleation potency by segregation onto TiB_2 surface. The grain refinement process should include nucleation, dendrite remelting and multiplication. Both of them play an important role on the grain refinement of aluminium. The effect of excess Ti was to form many small conglomeration zones and to promote the dendrite remelting and multiplication.

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