A MODEL OF GRAIN REFINEMENT MECHANISM FOR ADDING AL-TI-B MASTER ALLOYS INTO ALUMINUM

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ABSTRACT

Al-Ti-B master alloys have been used as grain refiner for Al castings for long time, although the mechanism, especially the role of boron in grain refining process, is not very clear till now. In this work, a model based on the study of some Al-5%Ti-1%B master alloys of different microstructures is suggested. According to this model, the $Al_{1-x}Ti_xB_2$ phase in Al-Ti-B master alloys is an additional nucleus for soid Al besides the Al_3Ti phase. The Ti released from $Al_{1-x}Ti_xB_2$ particles may help the nucleation of α-Al. Due to the surface energy between Al and $Al_{1-x}Ti_xB_2$, as well as the liquid agitation in Al melt, α-Al nucleates more easily in the grooves between the $Al_{1-x}Ti_xB_2$ particles of boride clusters than on the individual $Al_{1-x}Ti_xB_2$ particles.

Keywords: *Al-Ti-B, master alloy, boride cluster, grain refinement mechanism.*

1. INTRODUCTION

The grain refinement in Al after adding Al-Ti and Al-Ti-B master alloys which result in a final composition of at least 0.15 wt.% Ti, is due to the reaction (Al_3Ti + Liquid Al --> α-Al) at a few degrees above the melting point of pure Al[1,2,3]. When a piece of master alloy is immersed in liquid Al, the Al_3Ti particles introduced by master alloy immediately begin to dissolve. The dissolution rate depends on the size and morphology of the particles, and the dissolution time varies from a few seconds to half an hour according to different calculation methods[4]. Therefore, if the total Ti content is far less than 0.15 wt.% in Al melt, the grain refinement effect decreases with contact time, and it should disappear when all the Al_3Ti particles are totally dissolved. In practice the Ti concentration in Al melt after adding master alloys is usually only 1/30 to 1/15 of 0.15 wt.%. The boron additive in Al-Ti master alloys significantly changes the grain refinement behaviour. It is reported that a good refinement effect exists for more than 10 minutes contact time at about 750 ^oC for Al-Ti-B master alloys, and the grain refinement efficiency is strongly influenced by the Ti/B ratio[5,6]. Many theories have been proposed to explain the existence of grain refinement effect when Ti content is far less than 0.15 wt.% in liquid Al, and also the improvement of grain refining ability of Al-Ti master alloys by boron. The most important four are the phase diagram theory, boride-carbide theory, aluminide preservation theory and metastable boride theory.

According to the phase diagram theory[1,2,3,7,8,9,10,11], boron expands the range of the peritectic reaction (Al_3Ti + Liquid Al --> α-Al) by reducing the solubility of Ti in liquid Al. Therefore the peritectic point moves towards Al side and the peritectic reaction takes place at lower Ti concentration. The boride-carbide theory[6,12,13,14,15,16] suggests that α-Al can nucleate directly on TiB_2 particles or TiC particles. The aluminide preservation theory proposes that boride phase may protect Al_3Ti particles from fast dissolving, by that boride phase forms a shell surrounding Al_3Ti particle[17,18,19,20,21], Al_3Ti phase is preserved in borides cavity[22], and an absorption layer of Al_3Ti phase is formed on boride particle[23]. The metastable boride theory[4,24,25] is based on the assumption that a series of transformations (TiB_2 + Liquid Al --> $Al_{1-x}Ti_xB_2$ + Ti, Ti + Liquid Al --> Al_3Ti, Al_3Ti + Liquid Al --> α-Al) may take place in Al melt during the solidification process after Al-Ti-B master alloy is added. Through these transformations, Ti in a boride particle is released to Al melt and an Al_3Ti sheath is formed around the boride particle. The Al_3Ti sheath serves as nucleation site for α-Al when temperature is reduced. The observation of these transformations was reported by Schumacher in his studies of the crystallisation of amorphous Al alloys[26,27]. Although many studies address to the mechanism of grain refinement by using master alloys with different Ti/B ratio, i.e., with different compositions, it is found that Al-5wt.%Ti-1wt.%B master alloys produced by different producers, or by the same producer but in different batches, reveal quite different grain refining efficiencies[28,29]. In this work a boride cluster model is suggested to assess the influence of the spatial distribution of the boride phase in Al-Ti-B master alloys on grain refinement ability.

2. EXPERIMENT AND RESULTS

The grain refining efficiencies of three Al-5wt.%Ti-1wt.%B commercial master alloys, labelled 1, 2 and 3 with the same chemical composition, were tested at 750 °C and 840 °C in 99.7% pure Al leading to the final Ti content in Al castings being 0.25 wt.%, 0.05 wt.%, 0.02 wt.% and 0.005 wt.%, respectively. An Al-5wt.%Ti master alloy was used as reference. Fig. 1 shows the average grain sizes in the Al castings.

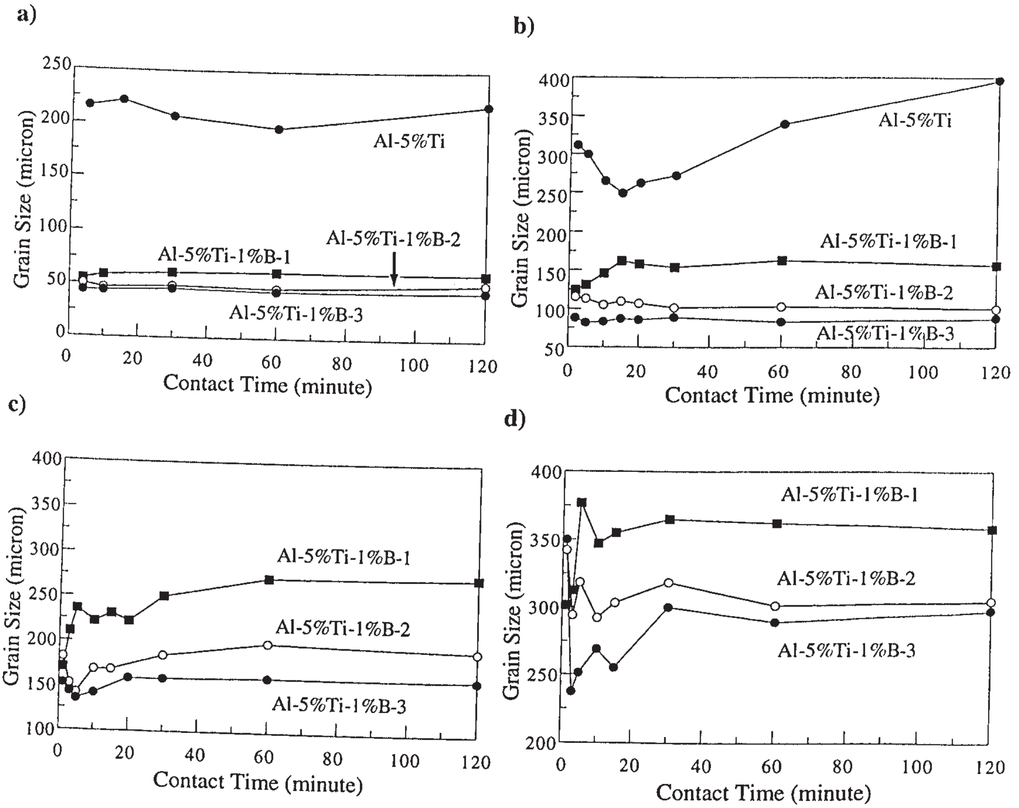

Fig. 1. The grain size of Al castings grain refined by Al-5wt.%Ti and three Al-5wt.%Ti-1wt.%B master alloys. The amount of added master alloys results in 0.25 wt.%Ti for a), 0.05 wt.%Ti for b) and 0.02 wt.%Ti for c) at 750 °C, and 0.005 wt.%Ti for d) at 840 °C in Al melt, respectively. The grain size of Al castings grain refined by Al-5wt.%Ti in c) and d) is over 800 μm, thus is not drawn in figures.

It is obvious that there are significant differences in the grain refinement efficiencies of the three Al-Ti-B master alloys. In order to trace the cause of these differences, the size, morphology and spatial distribution of the intermetallic phases in these master alloys, as well as the Al castings grain refined by these master alloys, were sophistically studied. In Al-Ti-B master alloys many $Al_{1-x}Ti_xB_2$ particles were observed to be in the form of clusters. A boride cluster consists of several $Al_{1-x}Ti_xB_2$ particles. Similar boride clusters were also observed at the centre of Al grains in the Al castings refined by Al-Ti-B master alloys, see Fig. 2. Furthermore, by optical microscope and SEM it is revealed that the tendency towards clustering is different for the three Al-Ti-B master alloys. The most effective master alloy shows the strongest tendency towards clustering, and the boride clusters in this master alloy are of the similar size, whereas the one with the most dispersed boride particles is the poorest grain refiner of the three, in both hypoperitectic and hyperperitectic conditions. The Al-5wt.%Ti master alloy lacking boron is much less efficient in refining Al grain than the three boride-containing master alloys. In hyperperitectic condition the grain refinement efficiencies of the Al-Ti and the three Al-Ti-B master alloys do not fade with contact time, whereas in hypoperitectic condition the efficiency of master alloy lacking boron fades fast, leading to a nearly natural grain size in Al castings after 60 minutes contact time. For details of the experiment and results, refer to [28] and [29].

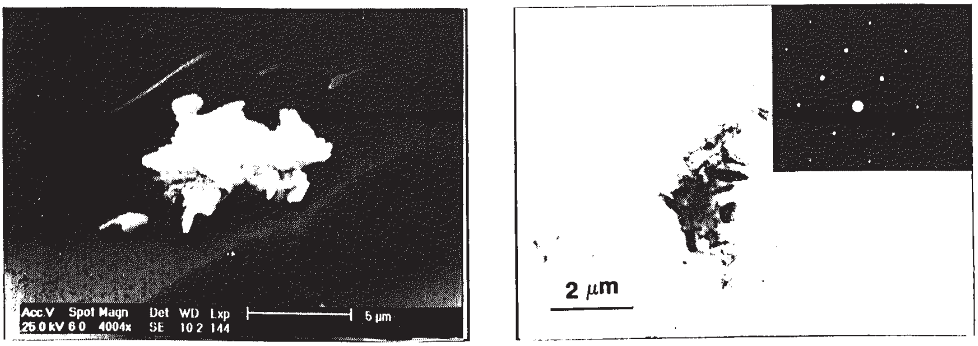

Fig. 2. SEM and TEM micrographs showing a typic boride cluster observed near the centre of an Al grain in the Al casting grain refined by Al-5%Ti-1%B-3 at 750 °C after 15 minutes of contact time, the Ti content in Al melt is 0.05 wt.%.

3. MODEL

Based on the observations a boride cluster model can be set up. In this model it is suggested that the boride clusters be effective nuclei for α-Al in both hypoperitectic and hyperperitectic conditions, to correlate the microstructure of more boride clusters of similar size with the better grain refinement efficiency. When the Ti content in Al melt is less than the peritectic point of 0.15 wt.%, i.e., in hypoperitectic condition, the process of the nucleation of an α-Al grain on a boride cluster can be shown in 2 steps as revealed by Fig. 3.

1. As a block of Al-Ti-B master alloy is added into Al melt, Al matrix of the master alloy melts immediately, and the boride clusters are then surrounded by liquid Al. The $Al_{1-x}Ti_xB_2$ particles in boride cluster react with liquid Al through reaction ($Al_{1-x}Ti_xB_2$ + Liquid Al --> Ti + $Al_{1-y}Ti_yB_2$), here $x>y$. Ti is therefore released to the Al melt and a Ti diffusion field around boride cluster is established. Due to the liquid agitation in Al melt, the released Ti diffuses rapidly and the Ti concentration around the boride cluster is not likely to be much higher than the average Ti concentration in Al melt. However, in some sites where the diffusion of Ti is hindered by morphologic factor, for example, in the grooves between $Al_{1-x}Ti_xB_2$ particles, or in other word, the bays in boride cluster, the Ti concentration may be somewhat higher than that of average.

2. When temperature is reduced, the heterogenerous nucleation of α-Al begins. Among the many potent heterogenerous nuclei, nucleation on a boride cluster demands smaller undercooling than on an individual $Al_{1-x}Ti_xB_2$ particle, because in those special sites such as grooves between boride particles, the increase of total surface energy during nucleation of a new phase is small. Furthermore, the high Ti content in these sites also increases the melting point. The morphologic factor hindering the diffusion of Ti generally also reduces the increase of total surface energy in phase transformation. Therefore, α-Al grain nucleates on the groove of the boride cluster and boride cluster becomes the most potent supplemental nucleus for α-Al besides Al_3Ti phase.

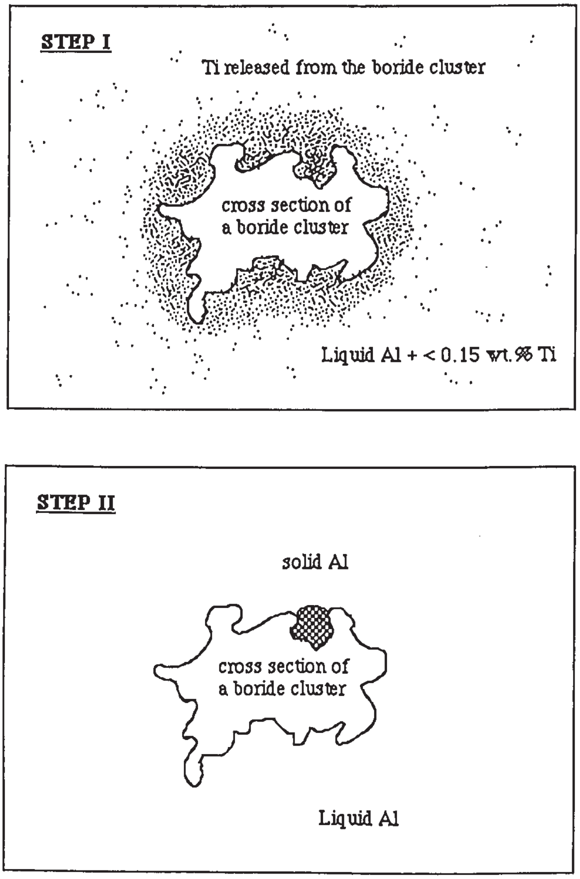

Fig. 3. Illustration of the mechanism of boride cluster model in hypoperitectic condition.

In hyperperitectic condition the average Ti concentration in Al melt is higher than the peritectic point, so the solid state boride phase suspended in the melt provides a large number of heterogeneous sites for the nucleation of Al_3Ti phase. This results in the easier formation, the more even distribution and the larger number of Al_3Ti particles in Al melt, which finally lead to the finer grain structure of Al castings. The irregular surface of boride cluster is still an advantage, but it is not so important as it is under hypoperitectic condition.

4. DISCUSSION

The three master alloys with boron are much better grain refiners than the one without boron. However, the master alloy without boron acts as a grain refiner if the Ti concentration in Al melt is above the peritectic point, and also below the peritectic point for short contact time. The grain refining effect of boron free alloy is attributed to the presence of Al_3Ti phase. The fading of the grain refinement efficiency below the peritectic point is expected, because of the dissolution of Al_3Ti phase after prolonged contact time. A dramatic improvement of grain refinement efficiency can be achieved by the presence of boron, and the efficiency in this case is little influenced by contact time. These facts suggest that $Al_{1-x}Ti_xB_2$ particles are quite inert. It is interesting to note that a master alloy containing only boron as an additional element, i.e. lacking Ti, does not act as a efficient grain refiner for the pure Al[30]. It is likely that the Ti released from $Al_{1-x}Ti_xB_2$ particles has contribution to the nucleation of α-Al. Our observations are qualitatively in agreement with the requirements that an effective grain refiner is obtained if the conditions of nucleation sites and the solute undercooling are fulfilled. When the nucleus of the smallest undercooling, for example, the boride cluster at long contact time in hypoperitectic condition, is active, the nucleation on other potent nulei such as the individual $Al_{1-x}Ti_xB_2$ particle is suppressed. However, the boride clusters of large size difference may demand different undercoolings for nucleating α-Al. Therefore, the existence of a large amount of boride clusters of similar size in Al-Ti-B master alloys is important. A small amount of boron in Al-Ti-B master alloys provides $Al_{1-x}Ti_xB_2$ particles. If several boride particles segregate during the manufacturing of master alloy, the boride clusters are formed. The boride cluster is a kind of supplementary nucleus besides Al_3Ti phase for α-Al in hypoperitectic condition, and both boride cluster and individual boride particle help the necleation of Al_3Ti particles which later nucleate α-Al grains in hyperperitectic condition. This may be one of the roles of boron in grain refining process.

5. SUMMARY

For Al-Ti-B master alloys used in industrial pure Al, composition is not the only factor determining the grain refining efficiency, although both Ti and B are necessary ingredients in an effective master alloy. There exist at least two kinds of potent nuclei in Al-Ti-B master alloys, the Al_3Ti particle and the $Al_{1-x}Ti_xB_2$ boride cluster. For the Al-Ti-B master alloys of the same chemical composition of 5 wt.% Ti and 1 wt.% B, the microstructure of more boride clusters of similar size leads to the better grain refinement efficiency, in both hypoperitectic and hyperperitectic conditions.

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