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Observation of crystal nuclei of aluminum refined by Al-Ti-B master alloy ①

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Abstract: The crystal heterogeneous nuclei of high purity aluminum refined by Al-Ti-B master alloy were studied by SEM and the mechanism of heterogeneous nucleation was discussed. It was found that the cluster of TiB_2 particles was in the center of grains, and a number of small protrusions were found on the surface of the particles. It was also found that the cluster was surrounded with the dendrites or circles enriched in Ti.

Key words: aluminum; heterogeneous nucleation; refining mechanism **Document code: A**

1 INTRODUCTION

The master alloy is usually used to refine the commercial aluminum alloy. As to the Al-Ti binary master alloy, Crossley[1] proposed the peritectic theory based on the peritectic reaction in the Al-Ti phase diagram as L + $TiAl_3$ = α (Al). The peritectic theory successfully explained the refining behavior of Al-Ti master alloy and it was well accepted by a lot of researchers[2,3]. With the presence of boron, Al-Ti-B master alloy has a well enhanced performance in the grain refining than Al-Ti master alloy. Since the factors affected solidification process were very complicated and almost all of the proofs were acquired indirectly, so various theories have been proposed to explain the refining mechanism of TiB_2 and many theories have been contradicted[4,5]. In this paper the crystal nuclei of aluminum refined by Al-Ti-B master alloy are studied and the refining mechanism is discussed.

2 EXPERIMENTAL

High purity Al(99.99%) 100 g was melted at 720 ℃, and Al-5%Ti-1%B master alloy was added as refiner, after held 20 min at 720 ℃, the melt was cast in cold steel moulds. The sample size was 40 mm in diameter and 55 mm in height. Metallographic samples of 10 mm thick were taken from the bottom of the sample, then it was electropolished and deep-etched with Keller′ agent to reveal the nuclei in the grains. The microstructure and composition of nuclei were investigated using JSM 6301F scanning electron microscope(SEM), with Link ISIS energy disperse spectrometry (EDS) and ATW2 window which can identify the elements with an atomic number greater than that of boron.

3 RESULTS

Fig.1(a) shows a number of the dendrites and circles appeared in the microstructure of samples. Fig.1(b) and (c) show these dendrites or circles had several contrasts and had the particles with a cavity at the center. Fig. 2 is the magnified image of nuclei. It was found that the nuclei were particle agglomerates not single particle, and the surface of particle was pockmarked with some small protrusions (Fig. 2(a)). The size of agglomerates of particle was normally 1 ~ 2 μm, but some of them varied up to 5 μm (Fig.2(b)). The particle had the hexagonal morphology with the diameter of 0.7 μm and the height of 80 nm, The size of the small protrusion varied

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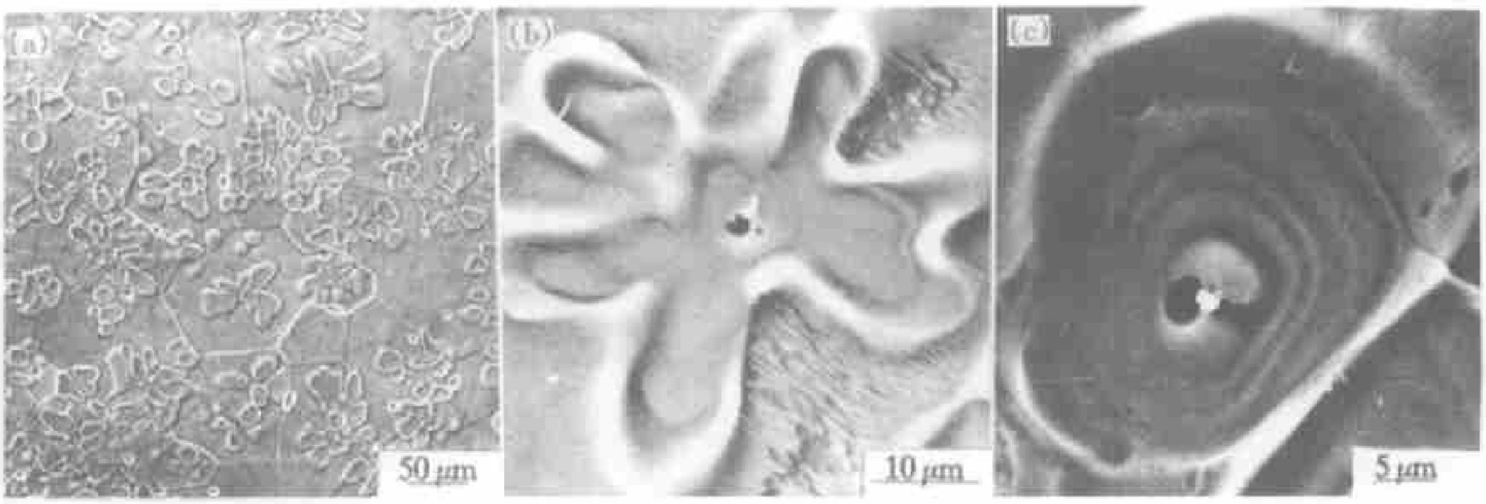

Fig.1 Grains with dendrites and circles after refining
(a)—Microstructure of α(Al); (b)—Dendrites with nucleus; (c)—Grain with circles and nucleus

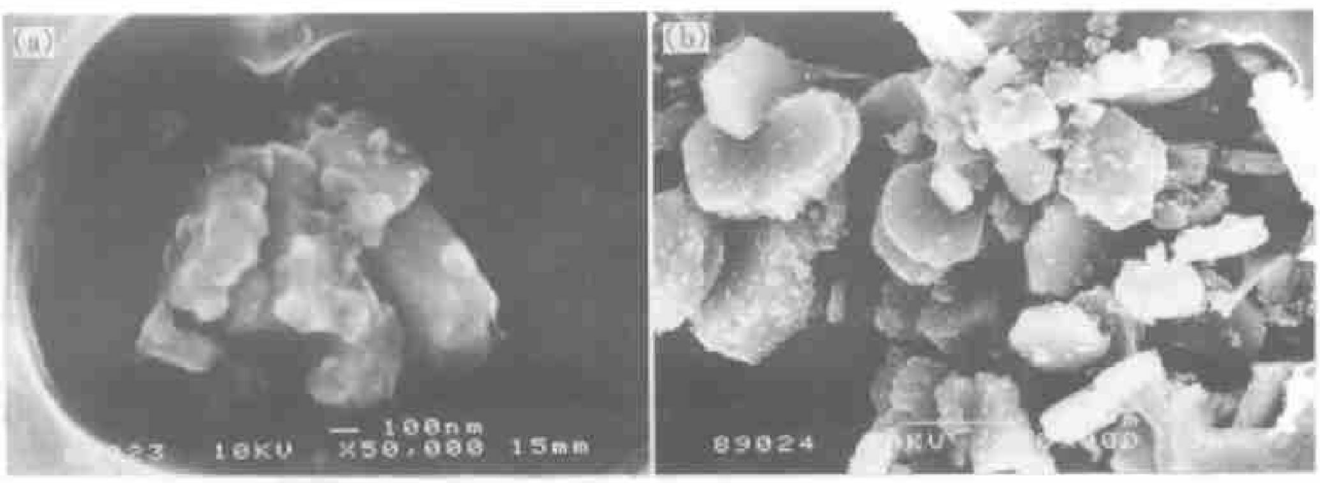

Fig.2 Heterogeneous nucleus of α(Al)
(a)—Nuclei with small protrusions; (b)—Image of nucleus

from 10 nm to 60 nm(Fig.2).

Fig.3(a) is the image of one nucleus (The white line shows the trace of the microprobe beam), Fig.3(b) is EDS line analysis results for B, Ti, Al respectively. It shows that the high Ti, B peaks and low Al valley are well correspond to the nucleus and it confirms that the small particles were enriched in Ti and B.

4 DISCUSSION

It is known that there are $TiAl_3$ and TiB_2 particles in the Al-Ti-B master alloy. When the Al-Ti-B master alloy is added into melt, the $TiAl_3$ particles are unstable and will be dissolved in a rate of 40 μm/min, whereas the TiB_2 particles are stable and will be acted as nucleant in the melt[6]. The explanations for TiB_2 promoting the refining efficiency could be categorized into two classes, (1) TiB_2 act directly as nucleant, (2) TiB_2 alters the phase relationships in the melt to improve nucleating.

Boride theory suggested that TiB_2 directly nucleated solid aluminum. The borides were hexagonal plates with lattice parameters of a = 0.3031 nm and c = 0.3029 nm[7]. Naess[8] have found the boride in the center of solid aluminum grains and established the orientation relationships between TiB_2 and α(Al) as (201)TiB_2 // (311)Al. However, Davis[9] found that TiB_2 was nonwettable with aluminum melt and was not an effective nucleant. With the purpose to prove whether TiB_2 alone can effectively nucleate solid grains of aluminum, Mohanty[10] success-

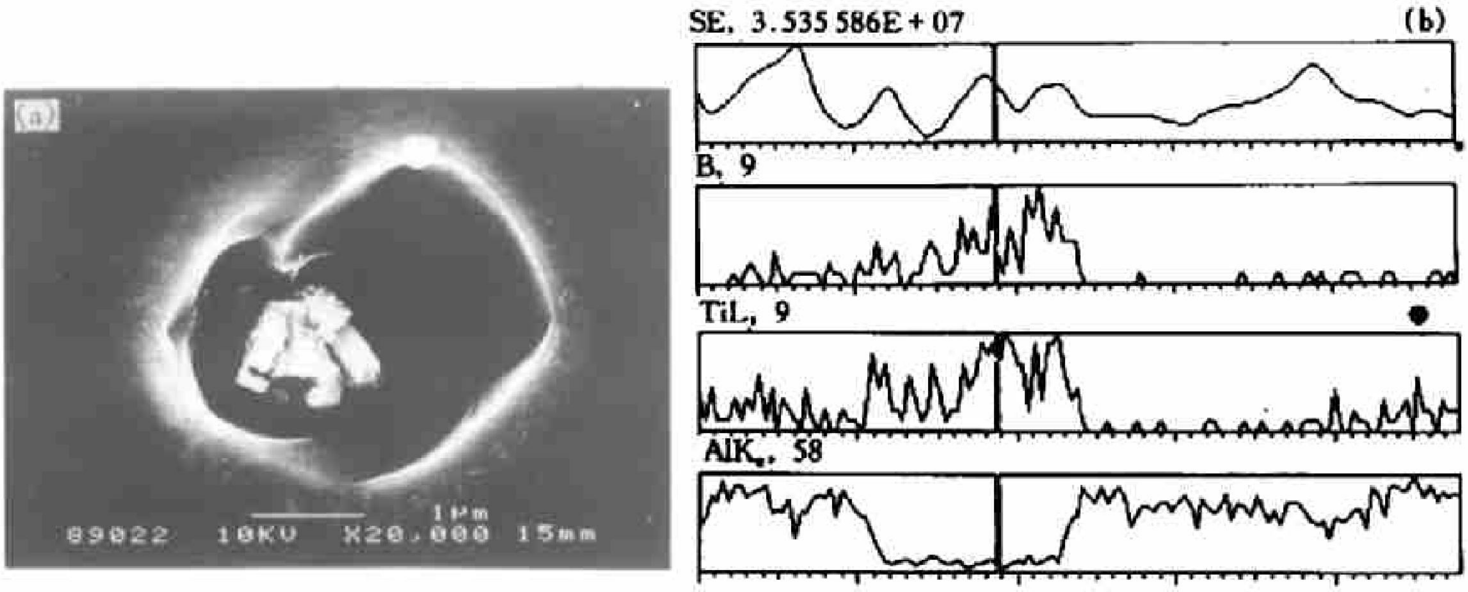

Fig.3 Image of nucleus and EDS line analysis results
(a)—SEM image of nucleus; (b)—EDS line analysis results for B, Ti, Al

fully introduced the boride crystals into aluminum alloy using a new technique and found that the TiB_2 particles alone were rejected by the solid/liquid interface and mechanically trapped at the grain boundaries, and that only when excess Ti was present, most of the TiB_2 particles were found within the grains. This means that TiB_2 alone can not nucleate α(Al) and Ti in excess of the stoichiometry of TiB_2 is a must for efficient refinement. Commercial and laboratory experience also show that master alloys having a 2.22 titanium to boron ratio (the stoichiometric value for TiB_2) are weak refiners and excess titanium is necessary for good grain refinement. So it lead to the theory that TiB_2 particles promote nucleation of other phase in the melts.

The proponents of phase diagram theories considered that $TiAl_3$ was effective nucleant. Based on this point of view, they proposed that TiB_2 increased the amount of $TiAl_3$. Davies[2] suggested that TiB_2 decreased the solubility of $TiAl_3$ and increased the amount of $TiAl_3$ particles in the melts. The suggestion is well account for the long period of fading, but it could not explain why the master alloy reacted very quickly and had more effective refining ability. Contrary to the proposal of Davies, Sigworth[11] and Moriceau[12] showed that the solubility of Ti in melt is about 0.4% at 775 ℃ and concluded that boron can not decrease the solubility of $TiAl_3$. Further more, Sigworth[11] and Marcantonio[13] proposed that TiB_2 nucleates $TiAl_3$ by a ternary monotectic reaction or ternary eutectic reaction, however, it was unfortunately that they both were hypothesis with no experimental evidence. Johnson[5] supposed the peritectic "hulk" theory which proposed that the formation of protective borides sheathes at the liquid Al/$TiAl_3$ interface which effectively protected the aluminide from dissolving, however, it is thermodynamically unfeasible. According to the peritectic hulk theory, once a peritectic cell is activated, its higher Ti concentration should be equilibrated with the melt and dissipated in the next melting process and the solidification should have no refinement effect. But it showed good refinement effects in the repeated solidification experimentally. At present, it is the key problem that how TiB_2 particles promote nucleation of other phase[14].

The nuclei observed in our experiment is the cluster of particles with small protrusions not single particle. As mentioned previously, the cluster of particles is more favorable to nucleation than the single particle with respect to the energy related in the nucleating process[2]. The small protrusions on the surface of boride might introduce more slits when the particles pack up in the cluster, it also play good role to the nucleation.

It is very interested that there are the dendrites or circles around the nuclei. Backerud[3] and Maxwell[15] also found this titanium-rich "halo" around the $TiAl_3$ particles in Al-0.6% Ti alloy and concluded it is the result of peritectic reaction $L + TiAl_3 \rightarrow \alpha(Al)$. Based on this point of view, the dendrites and circles around the boride particles in our experiment are the result of peritectic reaction, but there is no evidence suggesting TiB_2 reacting with liquid aluminum directly in the manner of $L + TiB_2 \rightarrow \alpha(Al)$. Jones[16] calculated the activity of Ti in the melt and in the TiB_2 inoculant and proved theoretically that there was a specific affinity of Ti segregation to the inoculation surface. Based on these results, we explain the circles are the result of peritectic reaction and the dendrites are circles grown in some certain orientation. Due to the specific affinity of TiB_2 particles, the Ti atoms in the melt would segregate to the TiB_2/melt interface, which lead to the high Ti content in the vicinity of the TiB_2, particularly in the grooves and silts of the cluster of particles. As the Ti content come to an extent, a thin layer of $TiAl_3$ precipitated on the surface of borides undergoes a peritectic reaction and nucleates the solid $\alpha(Al)$. The first formed $\alpha(Al)$ having high Ti content is engulfed by the new formed $\alpha(Al)$. Since it is difficult for the Ti to diffuse from inside to outside through the shell of the solid $\alpha(Al)$, the solid $\alpha(Al)$ has a gradient of Ti content and shows composition contrasts after etched, which looks like circles. We found the fact that the Ti content in the inner circle is higher than that in the outer one and this fact is well corresponding to our analysis. Recently, Schumaccher[17] showed that TiB_2 promoted nucleation only when there is a layer of $TiAl_3$ on the TiB_2 surface and that nucleation is only on the (0001) faces of the boride particles which have the similar characteristic of the aluminide faces. Also, there are orientation relationships between the phases, (112) $TiAl_3$ // (0001) TiB_2, (111) TiB_2 // (112) $TiAl_3$. Because the layer of aluminide will not exist after peritectic reaction, it is difficult to find the $TiAl_3$ layer and to define the orientation relationship. So the nuclei and the process of nucleation need further study.

5 CONCLUSION

The heterogeneous nuclei of grains in high purify aluminum refined by Al-B master alloy are the cluster of particles rich in Ti and B, the cluster is surrounded by dendrites or circles enriched Ti and some small protrusions are on the surface of the particles. The small protrusions play an effective role to nucleation.

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