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A Comparison of the Effects of Al-Ti-B Type Grain Refiners from Different Makers on Pure Aluminum

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Abstract

Al-Ti-B grain refiners are used by aluminum alloy casting manufacturers to reduce the grain size of castings. Both Al-5Ti-1B and Al-3Ti-1B are common Al-Ti-B grain refiners that are produced by several grain refiner manufacturers. The grain refining effectiveness with respect to time of four Al-5Ti-1B refiner samples from four grain refiner manufacturers and two Al-3Ti-1B refiner samples from two manufacturers was tested on commercial purity aluminum. Among the same type of grain refiners, the result of comparing grain refining efficiency from different grain refiner makers has been discussed in this paper. The composite particles of the grain refiner samples were observed by SEM and analyzed in an attempt to approach and understand the result of grain refinement under stirring.

Introduction

As a well-established process in the casting industry, grain refinement has been applied on various metals and alloys. It is an important and popular practice in the aluminum industry and it has been extensively investigated over the half of the past century[1]. Through research, more efficient grain refiners can be developed to enhance the mechanical properties and castability due to the reduced grain size.[1,2] With the additions of grain refiners, the formation of a fine equiaxed structure can be obtained by restraining the growth of columnar grains and by providing nucleation sites for new grains.[3]

Although the grain refining of aluminum with Al-Ti-B has been known to be beneficial to cast aluminum for decades and has been produced and employed widely by casting manufacturers, no clear statistics show the difference between the grain refiners from different producers. A series of tests was applied to study and compare the effects of four Al-5Ti-1B refiner samples from four grain refiner manufacturers and two Al-3Ti-1B refiner samples from two manufacturers on pure aluminum. Moreover, when looking at key particles existing inside grain refiners, the distribution and aggregation of those composite particles like $TiAl_3$ and TiB_2 were observed by a scanning electron microscope (SEM). The observation of samples is discussed and analyzed in this paper.

Mechanisms of grain refinement

As-cast metal grain size and geometry are controlled by the rate of nucleation and grain growth. Grain size is inversely proportional to the undercooling rate because of an increased nucleation rate[1]. There are two main reasons to manage the nucleation during solidification. The first is to promote grain refinement, which controls the scale of the microstructure.[4] The second is the mechanical properties and performance of the metal or metal alloy can be improved,[5,13] such as reducing cracking and decreasing shrinkage porosity.[2] High nucleation frequency increases the number of nuclei in metallic melts which generates grains of small size. Small grain size benefits metal producing processes because of an improvement in the material's mechanical properties, machinability, castability, and formability.[4] Therefore nucleation is critical to grain refinement while grain size control is critical to metal manufacturing processes.

According to Murty, some methods like melt agitation and vibration during solidification will also cause the formation of a fine equiaxed grain structure.[1] However, inoculation is the most popular method because it is very simple to apply. Inoculation consists of adding solid active nucleant substrates to liquid metal to get the formation of fine equiaxed grains,[5] and has been applied widely in the aluminum industry to refine grains for years.[6, 15] To be an effective grain refiner, small grain size is an important factor to consider. Moreover, shorter contact time and longer holding time both need to be satisfied when evaluating the efficiency of grain refiners.[1]

Compound particles existing in grain refiners, like $TiAl_3$, TiB_2, and AlB_2, influence the performance and efficiency of grain refiners.[1,14] Sigworth and Guzowski discussed how boron worked together with titanium as a powerful and effective role in grain refiners.[7,8] Both boride and aluminide particles can benefit heterogeneous nucleation by offering nucleating sites in solidification.[9]

Experimental methods

In this study two common grain refiners were added to commercial pure aluminum (99.8%). There were four Al-5Ti-1B (wt%) refiner samples from four grain refiner manufacturers and two Al-3Ti-1B (wt%) refiner samples from two manufacturers employed in the experiments. The Al-5Ti-1B refiner samples were from Hebei Sitong New Metal Co., Ltd. (ST), Nanjing Yunhai KB Alloys Co., Ltd. (YK), Shenzhen Sunxing Light Alloy Materials, Co., Ltd. (SL), and London & Scandinavian Metallurgical Co., Ltd. (LSM). The Al-3Ti-1B refiner samples were from Hebei Sitong New Metal Co., Ltd (ST) and London & Scandinavian Metallurgical Co., Ltd (LSM). ASTM E112 was applied to collect and analyze the data of grain size for each ingot.[10]

Table I. Compositions of CP Aluminum and Sample Refiners Applied in the Study in Weight Percent (%)

	Si	Fe	Ti	B	V	Others
CP-Al 99.8%	0.0568	0.091	0.004	0.0002	0.014	<0.04
YK TI5B	0.124	0.114	5.05	1.09	0.020	<0.04
ST TI5B	0.119	0.126	5.10	1.10	0.021	<0.04
LSM TI5B	0.093	0.132	5.04	1.06	0.014	<0.04
SL TI5B	0.145	0.140	5.12	1.06	0.018	<0.04
ST TI3B	0.101	0.123	3.13	2.02	0.024	<0.04
LSM TI3B	0.064	0.078	3.07	0.79	0.012	<0.04

*Aluminum% for each item is not listed in Table I

Approximately 5-kg commercial purity (CP) aluminum was melted and kept at a range of 715-725 °C in an induction furnace with graphite crucible. The melt was stirred thoroughly for thirty seconds after adding a solid grain refiner sample (0.2%) and then was allowed to stand for two minutes. Twenty ingots were cast from each melt: the first one was cast with no addition; the second to the sixth ingots were cast after the addition at 2, 4, 8, and 16 minute intervals; the 7th to the 20th ingots were cast every half hour after the 32nd minute. A thermocouple was applied each time before adding grain refiners and casting ingots and the crucible was washed by pure aluminum before each experiment.

Table II. Experiment Processing Timeline

- Sample 1 without any addition after the melt reaches 720°C
- Add grain refiner (30-second stir)
- 2-minute stand
- Time recount from 0 minute
- Sample 2 cast at the 2nd minute
- Sample 3 cast at the 4th minute
- Sample 4 cast at the 8th minute
- Sample 5 cast at the 16th minute
- Sample 6 cast at the 32nd minute
- Sample 7 cast at the 60th minute
- Sample 8 – 20 cast every half hour
- Sample 20 cast at the 270th minute

To cast the ingots, liquid aluminum was removed by a steel ladle from the metal bath and poured in preheated iron rings that were approximately 80 mm in diameter and the 35 mm in height. After two-minutes of cooling in room air, the ingot was quenched under tap water and demolded.

For microscopic examination of the casting, Keller's reagent was used as an etchant, which consists of 2 ml HF, 3 ml HCl, 5 ml HNO_3, and 190 ml distilled water[11]. Each ingot was immersed in the etchant for 10-15 seconds, washed in a stream of warm water, and then blown dry. The microscope used to observe grains in this study was a ZEISS Axio Imager A2m. SEM micrographs of sample grain refiners were taken also. Deep etching grain refiners required immersing samples in a solution of 250 ml of methanol containing 10 g of iodine and 25 g of tartaric acid for 4-5 hours[12].

Result and Discussion

It is known that the induction furnace affects the size of aluminum grains by vibration. The higher the power supply is, the stronger vibration produced, which will refine the grain size also. The grain refinement results are shown in Fig.1 in a logarithm time scale. The results of Al-5Ti-1B from the four different makers show no big difference in reaction time and grain size macroscopically.

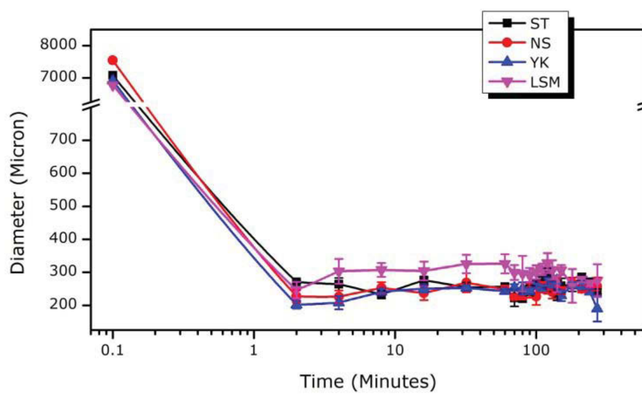


Figure 1. Comparison of experimentally measured grain size against holding time for adding Al-5Ti-1B grain refiner (Time at 0 minute means no addition of grain refiner) among four makers.

A close look of the comparison does show some variation in the diameter among the refiners. Overall there is no obvious difference among the products from ST, NS, and YK.

Figure 2 shows there is also small variation in the grain size between the two makers of Al-3Ti-1B, with the product from LSM functioning slightly better than that from ST-China. And by comparing the grain size in Figure 1 and Figure 2, Al-5Ti-1B refiners show better efficiency than Al-3Ti-1B.

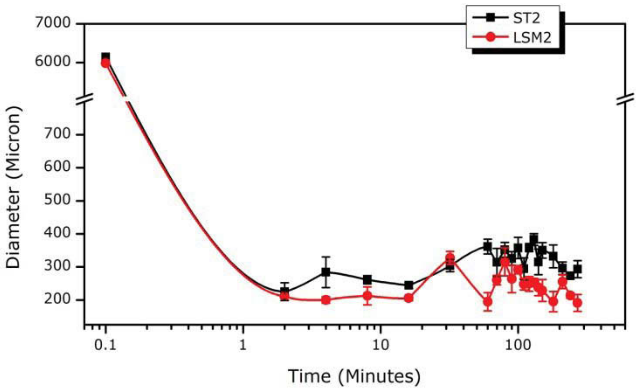


Figure 2. Comparison of experimentally measured grain size against holding time for adding Al-3Ti-1B grain refiner (Time at 0 minute means no addition of grain refiner) between two makers.

Flaky, blocky and petal-like shape $TiAl_3$ can be observed from featured SEM micrographs (Fig.4-Fig.8) of all the makers. These morphologies were observed in previous research on Al-Ti grain refiners by others, and their effects on grain refinement were discussed[11]. Large agglomerations of $TiAl_3$-TiB_2 particles are clearly visible in Fig. 3. Deep etch samples, Fig.4-Fig.8, revealed all large particles in the four grain refiners were a compound of $TiAl_3$ and TiB_2. The smaller TiB_2 particles were engulfed by the larger $TiAl_3$ particles, while most of the TiB_2 particles were pushed into the grain boundaries inside the grain refiners. Fig. 3 demonstrated that compounded TiB_2-$TiAl_3$ particles nucleated the aluminum grains in the grain refiners; TiB_2 particles themselves do not nucleate aluminum grains directly in the presence of large compounded particles of $TiAl_3$ and TiB_2. $TiAl_3$ particles also do not show the same capability in nucleating aluminum grains. They exist in the aluminum grain centers as groups of loosely clustered or compounded particles.

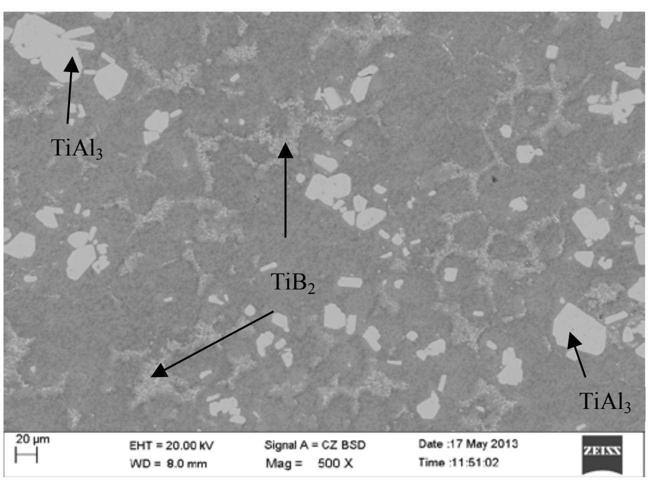


Figure 3. SEM micrographs of Al-5Ti-1B from maker ST-Baoding, China showing the morphological feature of TiB_2 and $TiAl_3$ particles with no etching.

Deep etched samples show the details of the compounded particles as TiB_2 particles with their surfaces partially exposed to aluminum rather than totally engulfed by the $TiAl_3$ particles. This finding suggests that TiB_2 does not nucleate $TiAl_3$. Instead of nucleating $TiAl_3$, TiB_2 particles were simply engulfed by $TiAl_3$ during formation right after the chemical reactions between a mixture of fluoride salts with molten aluminum. Present study also showed the existence of fluoride salts and Fe element, as contaminants, at the aluminum grain boundaries in association with TiB_2 particles. In comparison, the TiB_2 particles inside $TiAl_3$ particles are cleaner than those at the aluminum grain boundaries. It is therefore reasonable to believe that clean TiB_2 particles inside $TiAl_3$ particles have a higher tendency in grain refinement once added into aluminum melt, which is in agreement with previous studies[8].

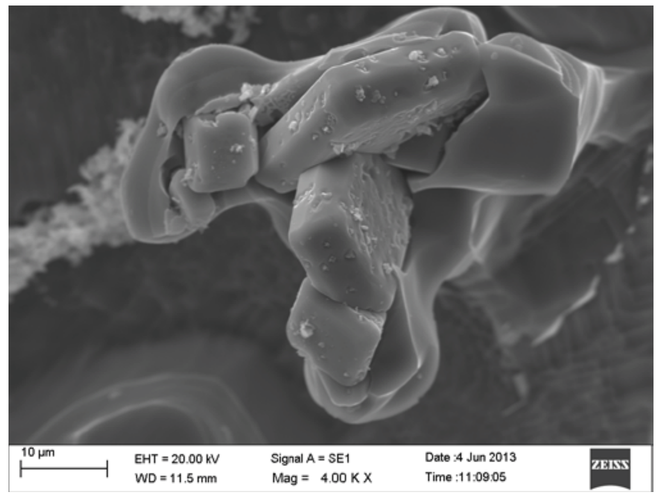


Figure 4. SEM micrographs of Al-5Ti-1B product from ST-Baoding, China

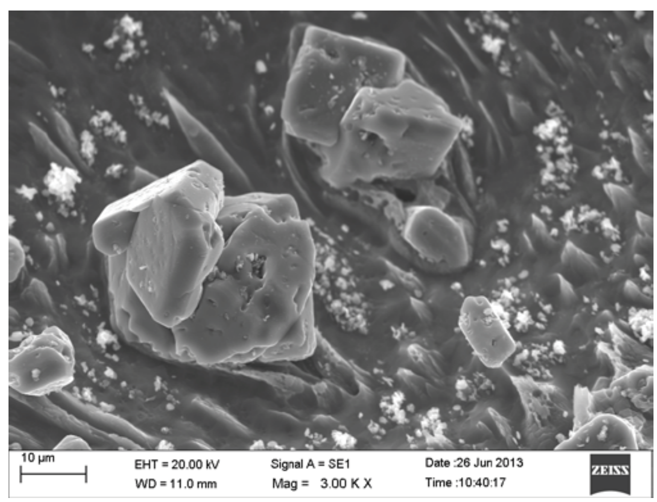
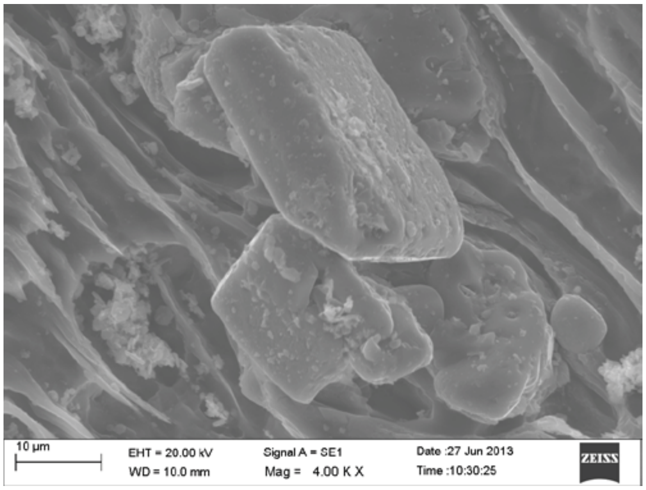
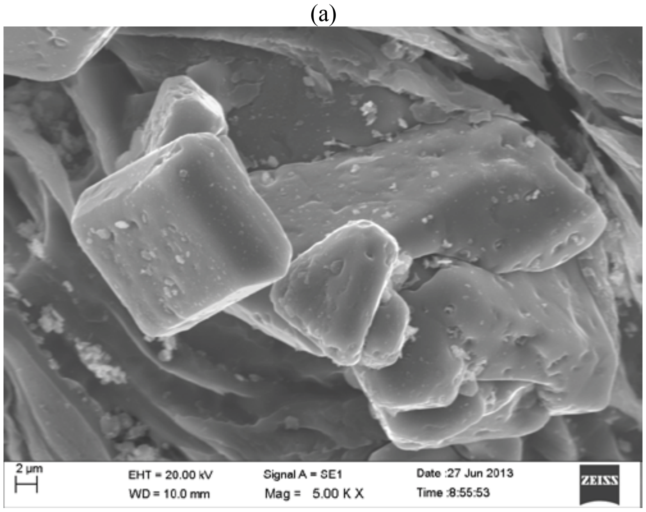


Figure 5. SEM micrographs of Al-5Ti-1B product from SL-Shenzhen, China

From the SEM micrographs of Al-5Ti-1B product from YK-Nanjing China, $TiAl_3$ is blocky and TiB_2 is engulfed inside the $TiAl_3$. There is not much difference compared to the product from ST-Baoding, China.



(a)



(b)

Figure 6(a), (b). Both SEM micrographs of Al-5Ti-1B product from YK-Nanjing, China

As shown in Fig.7, petal-like shape $TiAl_3$ is showing in Al-3Ti-1B product from ST-China. TiB_2 particles exist on the surface of $TiAl_3$ particles and are partially engulfed by the $TiAl_3$ particles.

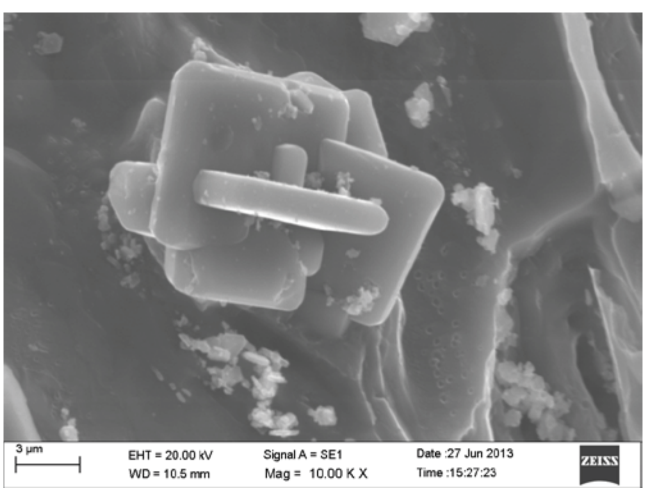


Figure 7. SEM micrographs of Al-3Ti-1B product from ST-Baoding, China

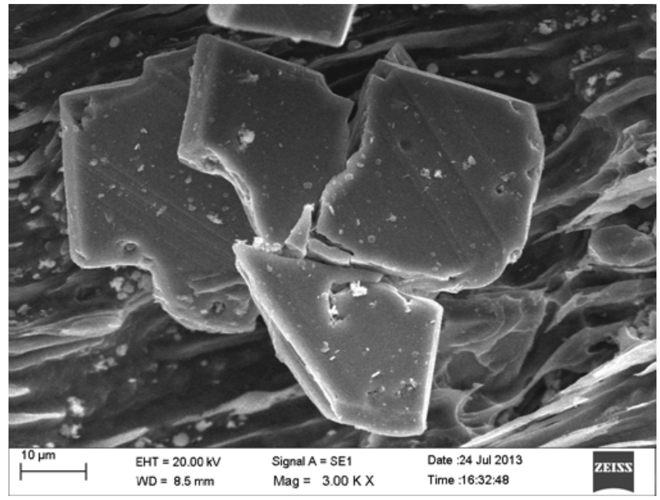


Figure 8. SEM micrographs of Al-3Ti-1B product from LSM

We can see small difference from Figure 9 (a)-(f), which presents comparison between two Al-3Ti-1B sample products at same holding time. The left of each picture is from LSM, with the right from ST-China.

(a) 2 minutes (b) 4 minutes

(c) 30 minutes (d) 90 minutes

(e) 120 minutes (f) 240 minutes

Figure 9. (a)-(f) Macrographs of comparison between two Al-3Ti-1B makers upon holding time (minutes). (L)-LSM; (R)-ST

The grain refinement effects of a grain refiner are related to the morphologies and compositions of the intermetallic particles, $TiAl_3$ and TiB_2. The former is larger than the later and dissolves into aluminum melt fast. TiB_2, in comparison, is smaller in particle size and stable in contact with aluminum melt. It is therefore believed that some TiB_2 particles nucleate $TiAl_3$ and then nucleate aluminum grains.[2] However, not all of the TiB_2 particles are active in nucleating $TiAl_3$ layers. It is believed that upon addition into aluminum melt only TiB_2 particles that are inside $TiAl_3$ particles in the grain refiners are active in nucleating $TiAl_3$ layers, which then nucleate aluminum grains.[8] Our observation revealed the existence of compounded $TiAl_3$-TiB_2 particles, with TiB_2 particles in similar sizes of a few micrometers, inside all grain refiners. The abilities in nucleating aluminum grains are therefore similar. Large particles settle down to the bottom of the melt faster than smaller particles when there is no stirring. Stirring by induction furnace does overcome the settling effects of the large $TiAl_3$ particles. As stirring is a common practice after the addition of grain refiners in the casting industries, the effects of the particles size of TiB_2-$TiAl_3$ are negligible.

Conclusion

There is no major difference among all the sample grain refiners from different makers, which might demonstrate the maturity and vitality of the development in manufacturing and processing techniques of common grain refiners. However, the small variation in grain size upon time also indicates the needs of optimizing the preparation technology parameters and manufacture process management.

The employment of an induction furnace in this experiment extended the grain refinement time and eliminated fading. This gives useful information to the casting companies that do not require a quick responding of the grain refiners, such as companies applying degassing and filtration after the addition of grain refiners.

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