Efficiency of different commercial TiBAI grain refiners on refinement of pure aluminum cast structures.

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Abstract. Industries largely rely on empirical tests to determine what composition and amount of TiBAI grain refiners to add during the casting of aluminum alloy for cast grain structure refinement. TiBAI grain refiners are aluminum master alloys having intermetallic particles within the aluminum matrix, these particles are mainly made of Ti and Al borides, having higher melting point than aluminum matrix. Addition of them to the melt, induces heterogeneous nucleation of aluminum cast grain structures, which promotes solidification of fine equiaxed grains at expense of columnar grain structures. This yields in grain refinement of cast structures, and is beneficial to mechanical and surface treatment properties on the final product. Very often in industrial practice during casting, whether a grain refiner is suitable for a given alloy, the amount to be added in the melt, and what cooling rates to use, are questions remain and reaching the balance becomes a cumbersome practice, and leads to pernicious material’s properties. This study aims to explore the refinement efficiency of three variants of locally supplied TiBAI grain refiners on the microstructure of cast pure aluminum (CPAl). A standard test method of TP-1 was adopted and the efficiency of TiBAI grain refiners was determined according to the average grain sizes. It was found that Al-3Ti-1B alloys from different suppliers yield different grain sizes, however, Al-5Ti-1B alloy has better efficiency than Al-3Ti-1B alloy system on CPAl material. The optimum holding time for CPAl melt at 750°C is 5 minutes to achieve a fine grain size.

1 Introduction

Aluminum is one of the most produced metals on earth, only exceeded by iron [1]. In today’s world, aluminum alloys are used in various engineering applications, such as automobile panel sheets and powertrain parts, kitchen utensils, aerospace and beverages packaging. Metal industries make use of grain refiners to refine solidification structures which improve the workability and mechanical properties of the final product [2]. This happens during casting stage of the metal, grain refiners are added to the liquid metal as a solid master alloy, containing fine intermetallic particles within the matrix of metal alloy. The intermetallic particles have melting point that is higher than the matrix of metal alloy. The matrix will melt
and dissolve in liquid metal, the fine particles are spread within the liquid metal. The intermetallic particles become easily uniformly distributed across the melt with the stirring effect by means of induction furnace stirring effect or using a graphite rod. These particles will then act as sites for the heterogeneous nucleation of α-Al during the solidification process. The process is called grain refinement, or inoculation. The grain refinement results in refined small equiaxed α-Al grains in expense of columnar cast structures [4]. This promotes homogenously distributed microstructures with improved and uniform mechanical properties to cast products with high wall thickness. The refined cast structures have a positive influence on subsequent metal treatment and enhanced surface and mechanical properties of the final product.

During the casting of aluminum, the most commonly used grain refiners are based on the Al-Ti-B master alloy system, containing titanium diboride (TiB$_2$) and titanium aluminide (Al$_3$Ti) particles within an aluminum matrix. They are normally known as Ti-B-Al grain refiners, and can have various amounts of Ti and B alloying elements. Industries largely rely on empirical tests to find out which alloy (chemical composition) to use and how much (amount) of TiBAl grain refiners to add to a given aluminum alloy for optimal grain refinement results. To strike a balance is key since very often excess grain refiner is added, frequent stirring and prolonged preheating of the melt to soak the grain refiners are used unnecessarily. All the mentioned parameters and the extra addition of grain refiner increases costs and needed resources while negatively affecting the mechanical properties of the final product. Longer holding time increases production cost and delays final product deliveries and negatively affects the properties of the material. The industry reported that different grain refiners vary in their ability to refine grains, and as such, they possess different efficiencies [5].

This study aims to explore the refinement efficiency of three different locally supplied Ti-B-Al grain refiners on commercial purity aluminum (CPAl) and determine the optimum type of Ti-B-Al grain refiner and residence time of grain refiner in the CPAl melt based on obtained average refined cast grain size.

## 2 Experimental Procedure

### 2.1 Materials

The grain refiner rods from three different local commercial suppliers were used in this study and their chemical compositions were given in Table 1 below. The grain refiners were labelled as GR-A, GR-B and GR-C as seen in Table 1 below. Commercial pure aluminum (CPAl) was used as melt charge and its chemical composition is given in Table 1. All the elements were reported in weight percentage (wt. %).

| Table 1. Chemical composition of the commercial pure aluminum (CPAl) and grain refiner rods used. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Elements | Si  | Fe  | Cu  | Mn  | Mg  | Cr  | Ni  | Zn  | Ti  | Sn  | B  | Al  |
| CPAl    | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 99.88 |
| GR-A    | 0.06 | 0.13 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 3.22 | 0.01 | 1.01 | 95.50 |
| GR-B    | 0.06 | 0.13 | 0.01 | 0.01 | 0.01 | 0.01 | 3.08 | 0.01 | 1.01 | 95.60 |
| GR-C    | 0.10 | 0.12 | 0.01 | 0.01 | 0.01 | 4.98 | 0.01 | 98.92 |

Where GR-A (grain refiner A), GR-B (grain refiner B) and GR-C (grain refiner C)
All materials were prepared according to Standard Test Procedure for Aluminum Alloy Grain Refiners (TP-1) and the test was carried out according to TP-1 standard procedure and outlined in the sub-section below [3].

2.2 Standard Test Procedure for Aluminum Alloy Grain Refiners (TP-1)

A clay bonded graphite crucible of 10 kg with a volume capacity of 3 litres, had its inner wall coated with a coating paste using paint brush. The coating paste was prepared by mixing an Isomol 316 powder, Graphite paste, Ethanol at a ratio of 2:1:2 respectively to form a thin coating paste. The coated crucible was air dried and CPAI metal weighing 2.5 kg was then placed in the crucible. The crucible loaded with CPAI was then placed inside a top bench loader electric resistance furnace (muffle furnace), see Fig. 1 below.

Fig. 1. The consumables, equipment including furnace and coated clay bonded crucible with CPAI metal blocks inserted in bench top muffle furnace.

The muffle furnace was programmed to heat from room temperature to 716±5 °C at a heating rate of 60°C/hour with crucible and CPAI metal inside. The furnace was given enough time to melt the CPAI metal for wash heat. After pouring out the heat wash, the crucible was placed back in the muffle furnace. A 5.5 kg Al metal was loaded into the crucible, and allowed to melt. The dross was skimmed from the surface using a graphite rod while ensuring minimum disturbance of the liquid metal.

Fig. 2. Tapping melt using coated and preheated steel ladle, the quenching step in ring water quench tank and TP1 Al cast sample.

A steel ladle with coated inner and outer walls preheated to 360°C was taken out from the oven and used to tap reference sample by submerging the ladle inside the liquid metal, held for 30 seconds and withdrawn vertically from the melt to ensure that ladle is filled to the
bottom of the notch. The filled ladle is then lowered vertically onto the retaining ring of the water quench tank, while ensuring that the bottom of the ladle is 25 mm submerged into the running water, see Fig. 2 above. Thereafter a reference sample was removed from the ladle, marked and reserved for the metallographic examination.

The grain refiner alloy, i.e. GR-A as its chemical composition maybe seen in Table 1, was added into the melt at 716±5 °C by stirring the melt using graphite rod until it has been dissolved after 30 seconds. The weight of added grain refiner alloy was determined according to equation 1 given below:

\[
\text{Weight of grain refiner to be added (grams)} = \frac{(\% \text{Ti desired}) \times (\text{Weight of melt})}{\% \text{Ti in Grain Refiner alloy}}
\]  

(1)

Note that the desired amount of titanium (Ti) used during the determination of the weight of grain refiner added was 0.01 wt% and the weight of the melt was 5.50 kg. After 2 minutes elapsed, the melt was stirred with graphite rod for 15 seconds before a sample was taken. The preheated steel ladles were alternated for each sample taken. Samples were taken after 2, 5, 10, 15, 20, and 25 minutes. All the cast samples were taken as it was done during taking the reference sample. The remaining melt was then poured into a cast iron rectangular mould that was coated and preheated under similar conditions to the steel ladles.

![Fig. 3. Cast samples withdrawn before adding grain refiner (1), after 2 minutes (2), after 5 minutes (3), after 10 minutes (4), after 15 mins (5), after 20 mins (6) and after 25 mins (7).](image)

All seven cast samples were marked accordingly and reserved for metallographic examination and grain size measurement.

### 2.3 Metallographic examination

A transverse section at 38 mm from the base as measured along the slope side was sectioned using a SiC cut-off wheel blade under water cooling, see Fig. 4. All the base parts were cold mounted in a resin.
Fig. 4. A diagram of cast sample showing examination plan, wet sectioning cast sample and sectioned cast samples through examination plane.

The mounts were plane and fine ground, thereafter polished to mirror surface finish according to the following steps, SiC papers #120, #240, for plane grind and #400, # 600 for a fine grind, the diamond lubricants of 9 um, 6 um, 3 um and 1 um on magnetic discs Mol and Nap (MD-Mol and MD-Nap) polishing cloths for mirror surface finish. The grinding and polishing parameters such as force, disc speed and time used were adopted from ASTM E 3-02 Metallographic sample preparation standard.

A Struers Lectro-Pol 5 electro-etching machine was set to, 25 volts dc, flow rate of 20 ml/min, current density of 5 A/cm² and electro-etching was done for 4 minutes using 1.8% HBF₆ electrolyte solution. The electro-etching technique used was Barker’s reagent solution. Sample surfaces were rinsed in tap running water and dried using compressed air, see Fig. 5 below of electro-etched samples.

Fig. 5. Image showing cast sample at cross-section surfaces after electro-etched with Barker’s reagent solution.

The mounts were examined and photographed under an optical light microscope (Olympus DSX50). The micrographs were acquired at two different magnifications, i.e. 139X and 277X, using polarised light mode and used to determine the average grain size.

2.4 Grain size measurement

The average grain sizes were determined according to an ASTM E 112-12 standard using the linear intercept method. The magnification of the micrograph used for the reference sample
was 139X and for added grain refiner alloy samples was 227X. The reason for using different magnifications is because the reference sample had a larger grain size but added grain refiner alloy samples had a smaller grain size. For the statistical analysis, 20 test lines were used, i.e. 10 test lines embedded horizontal and 10 test lines embedded vertical on micrographs with lengths ranging from 899.97 µm to 917.62 µm and at least 20 test fields were covered during the analysis of one sample.

The intercepts of grain boundaries with test lines were counted with the aid of Image J software and average linear intercepts were calculated, which were thereafter converted into average grain size and also into ASTM grain size number. The results were tabulated in Table 2 of Grain Size Analysis given in the results and discussion section.

**3 Results and Discussion**

In order to assess the efficiency of different grain refiner alloys, it is necessary to use commercial purity aluminum (CPAl) as a reference material. In fact, it has been frequently used as a reference material during the study of grain refiner alloys for the past years [2]. Fig.6 (a) shows micrograph of cast grain structures of CPAl solidified in the TP1 mould sample without the addition of the grain refiner. It reveals a completely coarse columnar grain structure, and will be regarded as the reference for a non-grain refined structure. The solidification of columnar grain structures is attributed to the lack of heterogeneous nucleation sites, which is provided by solid particles (e.g. TiB₂ and Al₃Ti) within the melt that provide nucleating sites during the solidification process and results in equiaxed grains structure [4]. Z. Fan et al reported that the edge of TP1 sample shows columnar grain structures while the central region of the sample shows equiaxed grain structure, suggesting that at some point of the solidification process a transition of columnar-to-equiaxed has occurred, as seen on cross-section micrograph given in Fig. 6 (a). This is misleading, since the vertical section of the similar TP1 sample shows a fully columnar grain structure [5]. The equiaxed grain structure morphology in Fig. 6 (a) is a result of sectioning of the columnar grains at the centre of the TP-1 sample. Unfortunately, there was not enough TP-1 sample to show the vertical-section micrographs hence only cross-section micrographs were reported.
Fig. 6. Macrographs showing cross-section of the cast grain structures of (a) commercial purity aluminum without the addition of grain refinery (b) with the addition of grain refinery, 5 mm scale bar.

Fig. 6 (b) shows the micrograph of the cast grain structure of CPAl with the addition of 0.32% of grain refiner GR-A (Al-3Ti-1B) alloy. It shows fine equiaxed cast grain structures as compared with Fig. 6 (a) of CPAl without the addition of grain refiner alloy. A similar observation was made on other grain refiner alloys GR-B (Al-3Ti-1B) and GR-C (Al-5Ti-1B) addition to CPAl. The detailed microstructural analysis to determine the average grain size as a function of time was carried out and the results were tabulated in Table 2 below and the graphs were plotted in Fig 8 for comparing the efficiencies of grain refiner alloys GR-A, GR-B and GR-C on the refinement of CPAl cast structures.

Fig. 7. (a) Optical light micrograph showing cast refined grain structures after addition of grain refiner (b) image showing interface of Image J that was used to determine average grain size, 500 µm scale bar.

The grain size analysis and measurement for CPAl without the addition of grain refiner were done on similar micrographs given in Fig. 6 (a) using image J shown in Fig. 7 (b). The
micrograph in Fig. 6 (a) was acquired by the stitching method at Mag 139X and an image with a scale bar of 5 mm was achieved. Similar processing was done to achieve Fig. 6 (b) for CPAI with addition of grain refiner alloy. This was done because the cast grain size structures were very large in such a way only two grains would fill the image at Mag 139X with a scale of 500 µm. But for CPAI with the addition of grain refiner alloy, analysis was carried out on micrographs given in Fig. 7 (a) on the image J platform shown in Fig. 7 (b). Fig. 7 (b) shows fine equiaxed grain structures that are homogenously distributed across the matrix, which pointed out that the Al-Ti-B alloy systems are effective in refining cast structures of CPAI materials.

Table 2. The average grain size of refined cast structures after the addition of TiBAI system grain refiner alloys determined by the linear intercept method using ASTM E 112-12 standard.

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Average Grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GR-A</td>
</tr>
<tr>
<td>0</td>
<td>1714</td>
</tr>
<tr>
<td>2</td>
<td>188</td>
</tr>
<tr>
<td>5</td>
<td>181</td>
</tr>
<tr>
<td>10</td>
<td>182</td>
</tr>
<tr>
<td>15</td>
<td>185</td>
</tr>
<tr>
<td>20</td>
<td>154</td>
</tr>
<tr>
<td>25</td>
<td>184</td>
</tr>
<tr>
<td>Average Grain Size</td>
<td>179.0</td>
</tr>
</tbody>
</table>

The results of average grain size shown in Table 2 above were used to plot the graphs as a function of time and are given in Fig 8 below. Fig. 8 shows that all the grain refiner alloys GR-A, GR-B, and GR-C were effective in refining the cast structures of CPAI material from above average grain size 15000 µm down to 188 µm, 123 µm and 118 µm respectively after 2 minutes of holding melt at 750°C before casting. It has been reported that when the grain refiner alloy rods are melted into the CPAI melt at 750°C, TiB₂ and Al₃Ti solid particles are introduced and dispersed into the melt where they will provide nucleating sites for α-Al grains during solidification [6, 7]. The nucleating sites initiate heterogenous nucleation which promotes columnar-to-equiaxed transition and resulted in fine equiaxed grain cast structures.
Fig. 8. Average grain size of commercial purity aluminum (CPAl) with the addition of 0.01% Ti of commercial GR-A, GR-B and GR-C, Ti-B-Al system grain refiner as a function of holding time at 750°C before poured for solidification process.

Grain refiner alloy C (Gr-C) effectively refined the cast structure down to 96 um while grain refiner A (GR-A) and B (Gr-B) managed 181 um and 137 um respectively at the holding time of 5 minutes, as maybe seen in Fig 8 above. This could be attributed to excess amount of Ti content in GR-C alloy which was higher than in Gr-A and GR-B as seen in Table 1 under material used section. It is well known that TiB₂ particles from Al-Ti-B alloy system are potent heterogeneous nucleation sites of α-Al grains. In addition, soaking a melt at 750°C temperature, permits Al₃Ti particles to dissolved and increase Ti solute concentration in the melt. The dissolution process results in facilitates grain growth restriction during solidification. This effect is assumed to be stronger in the case of Al-5Ti-1B, which in turn, results in better grain refinement. It has been reported that the formation of Al₃Ti monolayer on the surface of TiB₂ particle during the solidification of the inoculated alloy, increases the potency of TiB₂ particle for nucleation of α-Al grains, and that occurs in excess of Ti solute in the inoculated alloy melt which is mostly observed on Al-5Ti-1B alloy system, i.e. GR-C alloy [5]. GR-B alloy has shown better effectiveness than the GR-A alloy at 5 minutes as seen in the Fig 8 above.

The study reveals that further holding the melt at 750 °C for more than 5 minutes has no significant effect on cast structure refinement, instead, the grain size started to coarsen, as seen from 10 minutes to 25 minutes. This is attributed to the settling behaviour of grain refiners in CPAl melt when they reside in the melt for longer times, because the density of TiB₂ and CPAL are 4.5 g/cm³ and 2.3 g/cm³ respectively, therefore particle sink is expected to occur [8].
4 Conclusion

The study reveals that
- Al-Ti-B alloy systems are efficient grain refiners for refining cast structures of commercial purity aluminum (CPAl) material.
- Different Al-Ti-B alloy systems have different refinement efficiencies.
- The optimum holding time of Al-Ti-B alloy system in CPAl melt at 750°C is 5 minutes.
- GR-A (Al-3Ti-1B) and GR-B (Al-3Ti-1B) show marginal differences in grain refinement efficiencies but there is slightly better efficiency of grain refiner B compared to GR-A after 5 minutes of holding melt at 750°C.
- GR-C (Al-5Ti-1B) has shown greater efficiency than GR-A and GR-B at all time frames, its effectiveness can be attributed to the excess Ti content which improves the potency of TiB₂ by forming a monolayer of Al₁Ti on its surface. Increased Ti content also results in increased growth restriction during grain growth, which results in more efficient grain refinement.
- After 5 minutes of holding grain refiner alloys in the CPAl melt at 750°C, there is no further refinement of cast structures, grain size begins to coarsen instead of refinement.

5 Acknowledgment

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