The Impact of TiCAI™ and TiBAI™ Grain Refiners on Casthouse Processing

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Abstract

Al-3% Ti-0.15% C grain refiner has been in commercial use for over five years. It has seen use in a wide range of alloy systems and solidification process methods. A number of differences have been observed when compared to the traditional Al-Ti-B grain refiners. These include melt cleanliness, interactions with degassing and filtration systems, grain structure and surface appearance. Using state-of-the-art equipment at Companhia Industrial Fluminense [CIF] in Brazil, these issues have been assessed on a production scale level. A wide variety of different alloys have been cast on a wheel and belt caster and processed to wire. The addition point of the grain refiner was varied between before and after the degasser, all additions being made before a ceramic foam filter. The effect of the grain nucleating particles and their interactions with melt cleanliness equipment was studied.

Introduction

Al-Ti-C grain refiners have recently been the subject of intensive research efforts [1 to 6] involving collaboration between the aluminium industry, suppliers and academia. This has resulted in the availability of potent Al-Ti-C master alloys which are finding increasing commercial use. The earliest systems in which Al-3% Ti-0.15% C have found approval and replaced other grain refiners have been in aerospace [7XXX series alloys] applications [7]. There are several fundamental differences between the Al-Ti-C and Al-Ti-B systems [3]. These arise from different grain nucleation mechanisms and particle agglomeration behaviour. Al-Ti-B is thought to involve a superficial aluminide layer on the nucleating particles, TiB₂ [8,10], whereas Al-Ti-C does not [1,11,12]. In terms of grain refining potency, Al-Ti-C is considered more potent on the basis of the number of TiC particles added to the melt [13,8] (which is only 25% of the number of TiB₂ particles which would be added with a similar feed rate of an Al-3% Ti-1% B or Al-5% Ti-1% B grain refiner rod). Al-Ti-C grain refiners can be used in place of Al-Ti-B in most wrought alloys, though to achieve best results the casting temperature should be kept as low as possible [11,14 to 17]. A more uniform grain structure across the cast section has also been observed [13], providing potential benefits of more uniform eutectic phases, reduced homogenizing times, reduced segregation, more uniform properties and better surface appearance.

The major drive in the development of Al-Ti-C grain refiners has been to achieve less particle agglomeration compared to the Al-Ti-B system. TiB₂ agglomeration is thought to be caused by a number of factors [19 to 24], including the presence of halogens such as chlorine, particle collision, attachment to oxide films, surface adhesion by the aluminide layer and growth in filters. Direct evidence of lesser agglomeration in the Al-Ti-C system has been observed by reduced rates of filter blockage and in-situ measurements of particle/inclusion populations [5]. Melt fluidity and castability has been reported to be improved by Al-Ti-C, particularly in 5XXX series alloys where Al-Ti-B is associated with formation of thick oxides [5]. The use of Al-Ti-C has been shown to result in improved ingot surface offering the opportunity for reduced scalping costs. A further benefit reported is the resistance to poisoning by Zr and Cr in high strength alloys [25, 26].

Recycling behaviour of Al-Ti-C bearing materials has been studied extensively [19,27] and no adverse effects from commercial use or laboratory scale testing have been reported. To address many of these issues on an industrial scale, a widely ranging experimental programme was carried out at Companhia Industrial Fluminense [CIF]. Several different alloy types [1XXX, 5XXX, 6XXX] were processed, and experiments designed to assess grain refining potency and grain size distribution, segregation, metal cleanliness, degasser interactions, melt fluidity, surface finish and recycling behaviour.
Experimental Procedures

The casting experiments were conducted at Companhia Industrial Fluminense (CIF) in Brazil. The different alloys were poured from one tonne coreless induction furnaces. Metal was treated in-line using a rotary degassing unit. The gas used was a 97% argon and 3% chlorine mixture. After degassing, metal was passed through a 12 inch x 12 inch ceramic foam filter [30ppi], before casting a bar section on a wheel and belt caster and then rolling to wire of nominal diameter 9.5mm.

Two grain refiner types were used in the experiments; Al-3% Ti-1% B and Al-3% Ti-0.15% C. Their chemical analyses are shown in Table I.

Table I – Chemical Composition of Grain Refiners Used

<table>
<thead>
<tr>
<th>Grain refiner</th>
<th>Ti</th>
<th>B</th>
<th>C</th>
<th>Fe</th>
<th>Si</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-3% Ti-1% B</td>
<td>2.80</td>
<td>0.85</td>
<td>&lt;0.001</td>
<td>0.09</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>Al-3% Ti-0.15% C</td>
<td>3.02</td>
<td>&lt;0.001</td>
<td>0.12</td>
<td>0.12</td>
<td>0.03</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The addition level used was varied up to a level of 3kg/tonne [0.009% Ti] in line with general customer requirements and to examine the effect of different grain refiner levels. A widely ranging experimental programme was performed. The alloys in Table II were all included.

Table II — Aim Composition of Alloys Produced

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Si</th>
<th>Cu</th>
<th>Mg</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>0.36</td>
<td>0.14</td>
<td>0.16</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5052</td>
<td>0.20</td>
<td>0.10</td>
<td>-</td>
<td>2.50</td>
<td>0.25</td>
</tr>
<tr>
<td>5154-A</td>
<td>0.20</td>
<td>0.10</td>
<td>-</td>
<td>3.50</td>
<td>0.25</td>
</tr>
<tr>
<td>6201</td>
<td>0.30</td>
<td>0.60</td>
<td>-</td>
<td>0.65</td>
<td>-</td>
</tr>
</tbody>
</table>

The programme included the following:
1. AA1100 alloy with grain refiner added before degasser in first half of cast and after degasser for the second half. [Tests done for both grain refiner types].
2. AA1100 alloy with Al-3% Ti-1% B added in first half of cast and Al-3% Ti-0.15% C in second half [Test also done with Al-3% Ti-0.15% C first followed by Al-3% Ti-1% B].

Chemical Analysis

Chemical analysis disk samples and sections of cast bar were taken for each test condition, and testing performed using a spectrometer. The grain refiners were analyzed using inductively coupled plasma (ICP) optical emission spectrometry.

PoDFA

PoDFA tests were taken by sampling the metal stream from both before and after filter positions.

Degasser dross

Samples were taken from the dross build-up in the degasser at appropriate times during the tests to assess grain refiner particle loss in the degasser.

Filtration

Samples were taken from the used filters to assess build-up and agglomeration of particles.

Grain refinement

Samples were collected from the metal stream to assess grain size using the Alcoa Cold Finger Test[28]. Bar sections were also taken to assess grain size.

Gas content

The hydrogen level was monitored using Al-scan equipment.

Mechanical properties

Tensile tests were taken for each condition. The heat treatments used for each alloy are given in Table III.

Table III – Heat Treatments for Tensile Property Evaluations

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA1100</td>
<td>None</td>
</tr>
<tr>
<td>AA5052</td>
<td>Annealed 3 hours at 380°C, air cooled</td>
</tr>
<tr>
<td>AA5154-A</td>
<td>Annealed 3 hours at 380°C, air cooled</td>
</tr>
<tr>
<td>AA6201</td>
<td>Solution treated 1 hour at 500°C, water quenched, aged 4 hours at 145°C</td>
</tr>
</tbody>
</table>

Electrical conductivity

For AA6201 alloy, the electrical conductivity was assessed using Kelvin bridge equipment.
Casting
During production of some of the alloys, melt fluidity in the tundish was enhanced when using Al-3% Ti-0.15% C compared to Al-3% Ti-1% B. This was particularly the case for the 5XXX series alloys, a phenomenon observed previously under controlled conditions \[5\] and in industrial experience. The effect was also apparent for 6XXX alloys, but not noticeable for 1XXX alloys. The appearance of the cast bar surface was affected in a similar way. The 5XXX products in particular exhibited a shinier and improved surface finish.

On visual inspection of the bar, a segregation phenomenon was observed in the 5XXX alloys, with some elements positively segregating towards the top surface of the bar. Visual examination during casting suggested Al-3% Ti-0.15% C was beneficial in this respect compared to Al-3% Ti-1% B. This was confirmed by chemical analysis for Mg and Fe; Al-3% Ti-0.15% C produces 10% less segregation compared to Al-3% Ti-1% B. This effect was not observed to any degree in the other alloy systems studied.

Grain Refining
Grain refining results from the Alcoa test samples showed some clear trends. Directly comparing the addition point of the grain refiner; a finer grain size is achieved when the grain refiner is added after the degasser compared to before. This is illustrated by the samples in Figure 1 [for AA1100 alloy]. The Alcoa sample for Al-3% Ti-0.15% C added before the degasser shows some columnar grains in the structure. In contrast, with the same grain refiner added after the degasser there is a finer grain size and a fully equiaxed structure.

Figure 2 compares Al-3% Ti-1% B and Al-3% Ti-0.15% C grain refiners. These samples are taken from the same production batch of AA6201 alloy. The first half of the production used Al-3% Ti-1% B after the degasser and the second half used Al-3% Ti-0.15% C after the degasser. A finer grain size and almost fully equiaxed structure is achieved with Al-3% Ti-1% B. A slightly coarser structure [and more columnar grains] was observed with Al-3% Ti-0.15% C.

Figure 3 gives a similar comparison to Figure 2, for AA5052 alloy. In this case the Al-3% Ti-0.15% C alloy was used for the first half of the production. As in the previous case, both grain refiners were added after the degasser. The Al-3% Ti-1% B grain refiner again gives a finer grain structure.

For each of the conditions above, Figures 4 to 6 show the grain structure in the bar. Details for all of the Figures 1 to 6 are given in Table IV.

PoDFA Results
The inclusion values from the PoDFAs ranged from below 0.01 up to 1.8 mm/kg Al. Across the matrix of parameters tested there were no clear trends observed [between grain refiner type, addition point or measurement point]. To establish a clear trend, it is considered that a much greater depth of testing is required than could be performed in the current work. In addition, the use of LiMCA would also shed more light on possible effects.

Gas Content
The hydrogen content in all alloys was between 0.06 and 0.10 ml/100g. Grain refiner type had no effect on gas content.

Mechanical Properties
Tensile tests performed showed that the desired mechanical properties were comfortably achieved in all cases. The grain refiner used and addition point had no significant effect on the tensile properties achieved.

Electrical Conductivity
The electrical conductivity of AA6201 alloy was not affected by type of grain refiner used. Values of approximately 54 %I.A.C.S. at 20°C were achieved.
Table IV – Details for Grain Size Photographs Shown in Figures 1 to 6

<table>
<thead>
<tr>
<th>Alloy AA</th>
<th>Grain Refiner</th>
<th>Addition Level[kg/t]</th>
<th>Addition point relative to degasser</th>
<th>Alcoa Sample</th>
<th>Grain size[µm]</th>
<th>Comments</th>
<th>Bar Sample</th>
<th>Grain size[µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>Al-3% Ti-0.15% C</td>
<td>3</td>
<td>Before</td>
<td>1</td>
<td>1042</td>
<td>Coarse columnar</td>
<td>4</td>
<td>140</td>
</tr>
<tr>
<td>1100</td>
<td>Al-3% Ti-0.15% C</td>
<td>3</td>
<td>After</td>
<td>1</td>
<td>236</td>
<td>Equiaxed</td>
<td>4</td>
<td>&lt;120</td>
</tr>
<tr>
<td>6201</td>
<td>Al-3% Ti-1% B</td>
<td>1</td>
<td>After</td>
<td>2</td>
<td>174</td>
<td>Equiaxed</td>
<td>5</td>
<td>&lt;120</td>
</tr>
<tr>
<td>6201</td>
<td>Al-3% Ti-0.15% C</td>
<td>1</td>
<td>After</td>
<td>2</td>
<td>262</td>
<td>Some coarse</td>
<td>5</td>
<td>180</td>
</tr>
<tr>
<td>5052</td>
<td>Al-3% Ti-0.15% C</td>
<td>1</td>
<td>After</td>
<td>3</td>
<td>1265</td>
<td>Coarse columnar</td>
<td>6</td>
<td>220</td>
</tr>
<tr>
<td>5052</td>
<td>Al-3% Ti-1% B</td>
<td>1</td>
<td>After</td>
<td>3</td>
<td>179</td>
<td>Equiaxed</td>
<td>6</td>
<td>150</td>
</tr>
</tbody>
</table>

Discussion

The grain size evaluations have highlighted a number of features. Firstly, the Alcoa test samples have shown to be a reasonable predictor for the onset of columnar grains in the current work. Comparing figures 1 to 3 with their counterparts in figures 4 to 6 shows this in almost each case. However, the use of the Alcoa test as a predictor for grain size is not useful for the casting process used in this work.

Another feature observed for both grain refiner types [results shown for the Al-3% Ti-0.15% C grain refiner as these show the difference more clearly due to the coarser grain sizes] is the effect of grain refiner addition point. For each trial comparing addition before degasser and addition after degasser the same trend was observed. If the grain refiner is added before the degasser then the final grain size achieved is larger than if the grain refiner is added after the degasser. This effect is readily explained from the chemical analysis samples taken, as well as samples of the dross removed by the degasser.

Chemical analysis samples showed Ti [and B or C as appropriate] levels higher in the end product if the grain refiner was added after the degasser compared with before. It was possible to adjust conditions in the degasser such that losses were as high as 40%. Although industrial experience is that losses are not this great; non-optimized degassing can lead to significant loss of grain refiner particles in the degasser. Agglomeration of TiB₂ particles from Al-Ti-B grain refiners is known to occur in the presence of chlorine[19 to 22, 24]. The use of chlorine gas in the degasser has confirmed this in the present work. Samples of the dross taken from the degasser after treatment showed the presence of grain refiner particles. Although it is difficult to be quantitative on such samples, the overall assessment suggested more particles in the dross from Al-Ti-B grain refiner compared to the Al-Ti-C. Care should be taken in interpretation of this result as the number of particles introduced with Al-3%Ti-0.15% C is of the order of 25% of the number introduced with Al-3% Ti-1% B.

A further feature of the grain size evaluations is the comparison between use of Al-3% Ti-1% B and Al-3% Ti-0.15% C. As expected from the lower number of particles introduced,
the grain sizes achieved in using Al-3% Ti-0.15% C are higher than with Al-3% Ti-1% B. The current work also shows the onset of the columnar to equiaxed grain structure is different [Al-3% Ti-1% B performing better]. It should be borne in mind that this is specific to this process and relates only to grain size. Industrial experience indicates that similar addition levels are generally used when switching from Al-3% Ti-1% B to Al-3% Ti-0.15% C grain refiner. In addition, many other benefits can be achieved from such a change. Some of these are demonstrated in the current work, such as improved melt fluidity, reduced segregation and improved surface finish. Others shown in previous work[1 to 6], and realized in industrial applications, include potential for improved surface-critical products and resistance to Zr poisoning.

An improved uniformity of grain size with TiC compared to TiB2 has been observed previously[3] in round billet production. This is not the case for the bars produced in the current process used in the current work.

For AA1100 alloy, two casts were produced where the grain refiner type was changed half way through the production. The grain refiner was added before the degasser in each case. For one cast Al-3% Ti-0.15% C was used for the first half, and for the other cast Al-3% Ti-1% B was used for the first half. There were no adverse effects observed on switching grain refiner type half way through the cast, indicating that mixing two grain refiner particle types is not a problem. This confirms previous observations[3]. However the differences indicated earlier between the grain refiner types [such as particle loss in the degasser and grain size] can still be observed. In addition, the order in which the grain refiners were added during the same cast was of no real significance in terms of mixing of grain refiner types.

The previously observed effect of Al-3% Ti-0.15% C in producing a more fluid melt compared to Al-3% Ti-1% B has been confirmed in this work. In particular, it appears to have a markedly different effect on the 5XXX series alloys. The heavy oxide build up which can occur with these high Mg content alloys appears to be drastically reduced when using Al-3% Ti-0.15% C alloy. The benefits of this have been seen in the current work in terms of an improved surface finish on the cast bar. In larger slab sections this may also help in terms of metal recovery and productivity as reduced scalping could be realized.

The reasons for the difference between the grain refiner types in relation to melt and product surface appearance is still the subject of speculation. Comments from industrial usage of Al-3% Ti-0.15% C in 5XXX alloys confirm that the metal in the launder has a significantly different appearance. TiC particles appear to have a major beneficial effect on the interaction with, and ability to reduce the build up of, Mg oxides when compared to TiB2 particles. The present work also indicates a positive effect of TiC compared to TiB2 on segregation in these alloys. This may help lead to an explanation of these differences in behaviour. A difference in level of solute rejection between the grain refiner particles would explain these phenomena. If TiC particles are associated with a lower level of solute rejection when compared to TiB2, then the liquid ahead of the growth front would not be as enriched in, for example, Mg in 5XXX alloys. In effect, this would mean that less Mg is available as solidification progresses to form oxides, or to segregate to the last areas of the casting to solidify.

A comparison of grain structures with Al-Ti-C and Al-Ti-B has been documented previously[3, 29]. This work suggested that Al-Ti-C is more responsive to constitutional undercooling than Al-Ti-B. The current work tends to confirm this, albeit under markedly different processing conditions and grain structure types than previous work.

Conclusions

1. The production facilities at CIF can be used to provide a thorough study on an industrial scale of the impact of grain refiners in the cast house.

2. Al-3% Ti-0.15% C improves melt fluidity and finished cast appearance in comparison to Al-3% Ti-1% B in 5XXX series alloys in particular, but also in 6XXX alloys.

3. Under the processing conditions used at CIF, Al-3% Ti-0.15% C produces a coarser grain size than Al-3% Ti-1% B, however it introduces 25% of the number of particles. The benefits of TiC to uniformity of grain size previously observed for billet production are not confirmed for bar production in the process used in this work.

4. Positive chemical segregation to the top surface of the bar in 5XXX alloys is approximately 10% less when using Al-3% Ti-0.15% C compared to Al-3% Ti-1% B.

5. Grain refiner type has no significant effect on gas content, mechanical properties or electrical conductivity.

6. Mixing grain refiner types in the same casting has no major effects on castability, although differences indicated in previous conclusions can be observed. If grain refiner type is changed during the same casting, the order in which grain refiner is added is of no real significance.
Acknowledgements

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References

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