



Trends in Rod Addition Point Increase Demands on TiBAI Quality

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1. Introduction

The huge technical development drive of **METALLURG ALUMINIUM** has led to a deeper understanding in the aluminium casthouse. Backed up by world renowned quality, **METALLURG ALUMINIUM** has been at the forefront of assisting the industry to improve quality and at the same time to reduce costs. This is being achieved by adding high quality grain refiners after the filter.

Various factors in today's casthouse are driving leading quality companies to move the addition point of their critical TiBAl rod grain refiner. These factors include improvements in the technology to reduce defect levels in the casthouse. The technology of degassing and in particular metal filtration has seen marked steps forward. An increased appreciation of the potential negative interaction between these cleaning systems and the necessary particles added by the grain refiner has contributed to the trend of post filter TiBAl rod additions.

2. Grain Refiner Addition Point

The life history of refiner particles can be followed, starting from grain refiner manufacturing, where they are made in molten aluminium, which is then solidified as a master alloy. On introduction to molten aluminium in the cast house, they are then released from their solid aluminium matrix. They may be introduced to molten aluminium in a furnace, a launder, or elsewhere such as the entry port of a degassing unit or before a filter. However, the trend is to add high quality refiners after the filter.

3. TiB₂ Particle Agglomeration

Agglomerations of TiB₂ can cause end product quality problems in certain applications. This is because TiB₂ particles are relatively much harder than aluminium.

METALLURG ALUMINIUM has carried out many collaborative studies to show that the following are all potential causes of TiB₂ particle agglomeration:

- Grain refiner manufacture
- Surface energy minimisation (encouraged by stirring e.g. in a degasser)
- Adherence to oxide films
- Halides e.g. chlorine (as used in many degassers)
- TiAl₃ layer on TiB₂

4. Interactions in the Casthouse

As grain refiners are added at various points in the cast house, so their interaction at these different points should be considered.

4.1 Furnace Additions

Addition of grain refiner to the (melting and/or) holding furnace is carried out in some casthouses. A fading of the grain refining effect can be expected after approximately 20 to 30 minutes of holding as the TiB_2 particles settle. These will tend to agglomerate on the furnace floor over time. This results in poor efficiency in terms of the grain refiner, although it does mean the demands on the grain refiner quality are not high.

It should also be remembered that remelting/recycling aluminium which has been previously grain refined will suffer from similar effects.

4.2 Laundry Additions

This is one of the most common practices. In order to maximise the time for melting and dissolution processes, and also to encourage better dispersion of the refiner particles, it is common practice to add grain refiner rod at an angle against the molten metal flow. Another potential concern is that of the effect of mechanical disturbance or oxide pull in, but it has been demonstrated that this effect is negligible and can be discounted.

The metal flow rate in the laundry varies greatly between cast houses. However, in general the flow rate is sufficient that there are no problems of TiB_2 particles settling in the laundry. One notable exception however is the twin roll casting process, where in general the metal flow rate is relatively low. Settling of TiB_2 particles to the bottom of the laundry can be experienced in this process.

4.3 Interactions with Degassers

It is common practice to degas molten aluminium using a mixture of argon and chlorine. As the name implies the purpose of this treatment is to reduce the hydrogen content of the metal. However, a second purpose is to improve the metal cleanliness by flotation of inclusions to the surface to form a dross. As reported by several workers, a small percentage of chlorine in the gas mixture used provides benefits in terms of inclusion removal.

In light of the knowledge of the negative role of chlorine in the agglomeration of TiB_2 particles, the addition point of the grain refiner is worthy of consideration. It has been considered that adding grain refiner into the degasser entry point is of benefit. The turbulence of the metal in the degasser provides excellent conditions for melting the rod and rapidly distributing the grain refiner particles. However there is evidence of loss of grain refiner particles to the dross.

Of more serious consequence is that when degassing with chlorine the conditions are conducive to agglomeration of TiB_2 particles. Apart from the role of chlorine, the input metal is relatively rich in oxide films compared to the output metal. In addition, the metal turbulence inside the degasser encourages particle collisions. Individual cast houses have been able to demonstrate these effects using LiMCA technology. All of these issues would tend to suggest it is preferable to add grain refiner after a degasser rather than before it, particularly if chlorine gas is being used. This is dependent on the cast house layout however, as the addition point needs to also take into account the cleanliness of the grain refiner, and the time required for dissolution of $TiAl_3$ particles (see 4.5).

4.4 Interactions in Ceramic Foam Filters

Prof W. Schneider and others carried out an extensive programme on ceramic foam filter performance. In one part of this work the impact of adding a grain refiner based on the Al-Ti-B system was assessed. They concluded that if the incoming metal cleanliness was good then there was a minimal impact of the grain refiner on the performance of the filter. However, if there is an artificially high inclusion loading from the metal (achieved by deliberately vigorously stirring the metal in the furnace), then the introduction of the grain refiner leads to a reduction in filtration efficiency. In such a case there was a disproportionate release of inclusions from the filter compared to the incoming inclusion levels. They assumed that the particles exiting the filter are agglomerates of inclusion species arising from the furnace metal interacting with particles from the grain refiner.

Metallographic evaluation of used filters suggests that the bridges of inclusions across the filter cell junctions, as seen in the absence of a grain refiner, do not appear when grain refiner is used. It has been suggested that the mechanism of filtration of a ceramic foam filter is altered in the presence of a grain refiner addition. The presence of a grain refiner from the start of casting appears to prevent the formation of bridges within the filter structure. The introduction of a grain refiner part way through the cast results in the destruction of any previously formed bridges. It should be made clear that these effects were observed for conditions where the metal inclusion level was artificially high. Under normal conditions the work concluded that the grain refiners have minimal impact on the filter performance.

4.5 TiAl₃ Dissolution

If grain refiner rod is added before a filter, then the time required for full dissolution of TiAl₃ particles needs to be considered. It is known from practical experience that if the rod is added too close to the filter, the filter can become rapidly blocked (or “blinded”) by TiAl₃ particles that have not dissolved in time. On addition of the rod to the launder, the aluminium matrix of the Al-Ti-B refiner has first to be melted to release the TiB₂ and TiAl₃ particles into the flowing metal. Once released into the molten metal the TiAl₃ particles can then start the dissolution process. The potential impact of partially dissolved TiAl₃ particles, on either filter performance or (in the case of grain refiner additions after the filter) product quality, has also been considered by various workers. One approach was to add grain refiner into a launder of flowing molten aluminium, and to move the position of LiMCA heads within the stream. This approach assumed that once there was no change in LiMCA response when moving the LiMCA head further away from the rod addition point, that all the TiAl₃ particles had dissolved. This work established that at the typical metal temperatures and flow rates in the launder in a cast house, the Al-Ti-B rod requires approximately one minute to melt and for all the TiAl₃ particles to dissolve. Another approach was to add a specially produced Al-0.7%Ti rod (containing TiAl₃ particles but no TiB₂) to try to measure the effect in a similar way. This special rod was added 4.5 metres upstream of a ceramic foam filter (giving a residence time of approximately 1.5 minutes). The work concluded that for rod added this far upstream of the filter there was no effect on filter performance. In other words all the TiAl₃ particles had dissolved between rod addition point and the filter.

4.6 Interactions in Deep Bed and Tube Filters

Deep bed filters are widely used in the aluminium industry to remove inclusions from the liquid metal. The inclusions are trapped in the pores on the surface of the solid granular (collector) medium. An important issue is the stability of the inclusion attachment, as the inclusions can be re-entrained by the flow of liquid metal. This feature can happen readily during the start up or stopping period. The changing metal flow rate can produce different flow patterns inside the

cavities between the collector elements, facilitating the re-entrainment of the already deposited inclusions. The character of the flow between the collector elements also influences the transport of inclusions toward the collector surface.

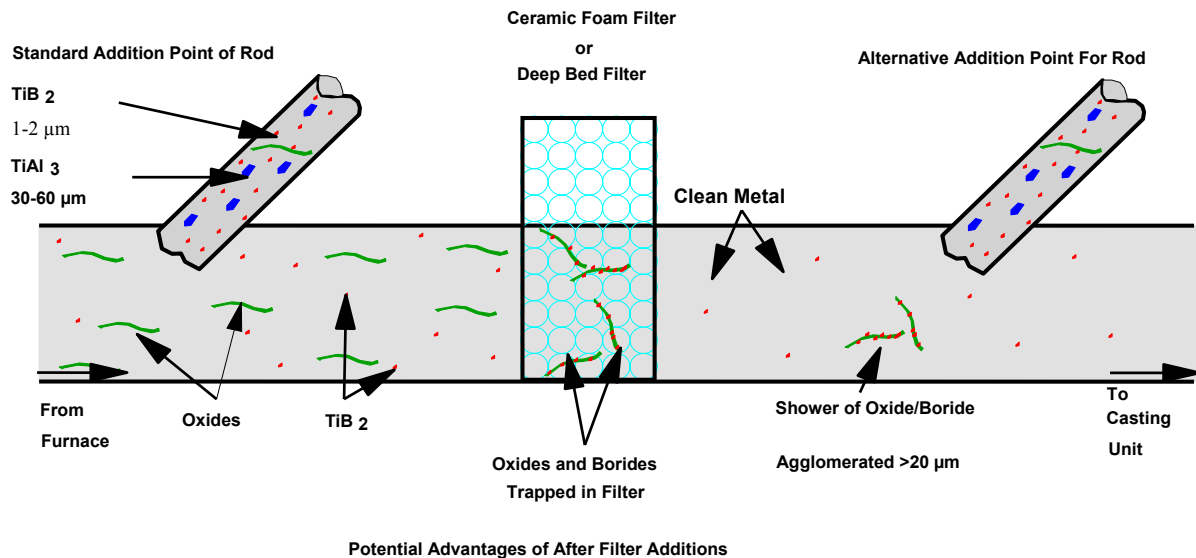
There have been studies on the effects of long time exposure to liquid aluminium of grain refiner particles, by examining used tube filters, which had been in extended production use. The thermal cycles and/or the extended quiescent periods during the lifetime of a tube filter can be critical. Under these circumstances, there is a transformation of the trapped TiB_2 particles into $(Ti,V)B_2$. Subsequent growth of such particles can then lead to the formation of more complex agglomerates and bridging within the filter, and so impair filtration efficiency and filter life.

5. Post Filter Addition

As the understanding of the interactions described has improved, so the drive to add post filter has gathered momentum.

Considering first the degasser, it is suggested that provided there is sufficient time for $TiAl_3$ dissolution before the next in line melt treatment (e.g. a filter) or casting (in the case of no filter), then rod addition after the degasser should provide benefits. Even if no chlorine is used in the degasser, there is still likely to be both some particle loss in the dross and some particle agglomeration.

Due to concerns over the cleanliness of grain refiner alloys (which could contain salt, oxide films, boride defects or agglomerations of these) they have traditionally been added before filters. However it is clear that filters remove some of the required nucleant particles from the metal stream. Addition of grain refiner after the filter might thus permit lower grain refiner addition rates.



In the normal situation, metal (including oxide films, and if recycled material is used also borides) flows along the launder and rod is traditionally injected before the filter. The rod adds aluminides, which dissolve within one minute, borides, which do not dissolve, and some oxide films. The oxide films (from the furnace and the grain refiner) and borides pass to the filter, where the oxide films are trapped along with some borides. The loss of borides in a filter system is considered to be mostly by adherence to oxide films, which the filter has trapped.

The remaining borides pass through the filter along with the Ti in solution to perform the grain refining. The metal after the filter is relatively clean, compared to the metal entering the filter. There has been ample evidence in the industry of showers of borides being released from a filtration system. These can be caused by changes in the metal head and hence pressure, or by vibrations or accidental tapping of the filtration assembly. A shower of oxide films decorated by TiB_2 particles is a potentially damaging defect. This is the likely cause of many of the defects found in thin foil and bright trim products.

If the quality of grain refiners is sufficiently high such that they can be added after the filter, then these showers of defects can be eliminated. In addition the loss of borides in the filter system would not occur, so less grain refiner would need to be added.

6. Conclusions

Although it has taken many years of technical effort and resource, the understanding of the effects of grain refiners and their particles has grown in depth by orders of magnitude. In combination with advances in metal cleaning technology, it has driven the industry towards improved quality at lower cost by adding high quality grain refiners after the filter with confidence.

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