International Journal of Modern Engineering Research (IJMER)
www.ijmer.com Vol.2, Issue.4, July-Aug. 2012 pp-2724-2727 ISSN: 2249-6645

Review of the Latest Developments in Grain Refinement

Lakhwinder Singh[1], Geetesh Goga[2], Rupinderpreet Singh[3]
Mechanical, K.C.College of Engg. & I.T./ PTU, India[1,2,3]

ABSTRACT: *There have been a number of studies in recent years relating to the mechanisms of grain refinement of Al-Ti-B refiners. Grain refinement of Aluminium and its alloys is a common industrial practice. The field has been investigated by many workers over past 60 years, not only to develop efficient grain refiners for different aluminium alloys, but also to achieve an understanding of the mechanism of grain refinement. There have also been studies on the interaction of refiners in the cast house environment. More recently there have been several new grain refining products introduced, which have been the subject of their own studies. These new refiners have a number of specific beneficial attributes, which distinguish them from the traditional Al-Ti-B refiners. The characteristics of the expanding family of refiners are reviewed, and their benefits explored in terms of these characteristics. The paper also aims to give an overview of the grain refiners available and guidance on their choice in different alloy systems and processing applications.*

Keywords: *Aluminum, Boron, Grain refinement, refiners, Titanium*

I. INTRODUCTION

It is well known that metals and alloys usually solidify with coarse columnar grain structure under normal casting conditions unless the mode of solidification is carefully controlled. It is possible to develop fine equiaxed grains in the as cast structure either by increasing the number of nucleation sites or by grain multiplication. McCartney has defined grain refinement as deliberate suppression of columnar grain growth in ingots and castings and formation of fine equiaxed solidification structure throughout the material. It is known that the grain size is inversely related to the degree of undercooling due to an increased nucleation rate. In other words, fine grains can be achieved by fast cooling that ensures a high degree of undercooling. Chemical grain refiners based on Al-Ti-B are widely used in aluminium casthouses and foundries worldwide. They are a key part in improving casthouse productivity, allowing faster DC ingot casting speeds, resistance to hot-cracking, as well as improving surface finish and mechanical properties. The pioneering work of Cibula on grain refining started in the early 1950's. This lead to the first industrially used grain refiners based on the formation of TiB_2 particles in situ in the melt via the addition of KBF_4 and K_2TiF_6 salts. However, this method suffered from rapid fade of the refining effect due to particle settling. The master alloy approach gave benefits in terms of providing 'readymade' TiB_2 particles of a more controlled and optimised size. A major breakthrough in the development of the use of refiners came with the availability of the alloy in rod form, first used in the mid 1960's. This allowed grain refiner additions to be made outside the furnaces, thus further reducing the fading effect of furnace additions and also the effects of 'poisoning' in certain alloy systems; this allowed much lower addition levels to be made and a more consistent grain refining performance to be achieved. Adding rod outside the furnace put a greater emphasis on the need to develop refiners with clean microstructures; the major features to be addressed were to reduce boride agglomerations, oxide films and residual fluoride salts. Rod is nowadays the most commonly used form of grain refiners, accounting for over 80% of grain refiner usage.

For many years the range of grain refiners available was mostly limited to three compositions all based on the Al-Ti-B system; namely Al-5%Ti-1%B, Al-3%Ti-1%B and Al-5%Ti-0.2%B. The Al-5%Ti- 1%B was, and remains, the most popular composition due to its high refining potency. The lower Ti content Al-3%Ti-1%B refiner was developed to meet the requirements to have a potent refiner, but not to exceed melt Ti specifications, which could be exceeded especially in plants with a high level of recycle. The lower B content refiners are used more specifically for production of surface critical products, to help reduce or eliminate the number of boride defects in the end product (simply by introducing fewer boride particles). The quality of Al-Ti –B grain refiners available in the market steadily improved in terms of cleanliness, grain refining effectiveness and especially consistency, during the 1980's and 90's.

With the ever-increasing demands on the quality of surface critical applications, an intense period of development in the mid 1990's resulted in the introduction of Al-3%Ti-0.15% C grain refiner. The Al- Ti-B quality development took place over a 40 year period – this was effectively matched by a concentrated development period of just a few years for the Al-Ti-C system. Whilst this refiner has penetrated a relatively small proportion of the market, it has proved to give benefits in terms of reduced particle agglomeration behaviour, resistance to poisoning by Zr (for 7xxx alloys), and better surface finish in 5xxx series alloys.

II. REFINER PARTCLE CHEMISTRIES AND TYPES

The nominal chemistry and particle types of the main refiners used in the aluminium industry are summarised in Table I.

Refiners	% Ti	% B	% C	% Sr	Borides	Aluminides
Al-5%Ti-1%B	5.0	1.0	0	0	TiB_2	TiAl3
Al-3%Ti-	3.0	1.0	0	0	TiB_2	TiAl3

1%B						
Al-5%Ti-0.2%B	5.0	0.2	0	0	TiB_2	TiAl3
Al-3%Ti-0.2%B	3.0	0.2	0	0	TiB_2	TiAl3
Al-3%Ti-0.15%C	3.0	0.0	0.1	0	TiC	TiAl3
TiBloy	1.6	1.4	0	0	$(Al,Ti)B_2$	-
Strobloy	1.6	1.4	0	Up to 10	TiB_2, SrB_6	**$SrAl_4$**

Note: International standards deliberately allow a higher Ti (up to 3.4%) and lower B (down to 0.7%) content than indicated. This is to encourage a superior boride microstructure.

Table I: Summary of Refiner Particle Chemistries and Types

III. TiBAl ROD ADDITIONS IN A TYPICAL DC CASTING SITUATION

On addition of the rod to the melt, the Al matrix of the Al-Ti-B refiner melts releasing the TiB2 and TiAl3 particles into the flowing metal.

3.1 Degassing*:*

If chlorine is used the conditions are conducive to agglomeration of TiB2 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. Many individual casthouses 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 casthouse layout, however, as the addition point needs to also take account of the cleanliness of the grain refiner, and the time required for dissolution of TiAl3 particles. It is suggested that provided there is sufficient time for TiAl3 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.

3.2 Filtration*:*

An extensive programme on ceramic foam filter performance has been carried out in Europe [1]. If the incoming metal cleanliness is high then there is 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. If grain refiner rod is added before a filter, then the time required for $TiAl_3$ particles to dissolve 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 undissolved $TiAl_3$ particles. Studies [2] 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 found that the thermal cycles and/or the extended quiescent periods during the lifetime of a tube filter can be critical. Under these circumstances, it was observed that there was 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.

3.3 Addition point:

Due to concerns over the cleanliness of grain refiners, they have traditionally been added before filters. However filters remove some of the required nucleant particles from the metal stream, so addition of grain refiner after the filter might allow lower 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 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 (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. There has been ample evidence in the industry of showers of borides being released from a filtration system, 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, and is the likely cause of many of the defects found in surface critical 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.

In the foundry situation there are many types of operation done in many different ways [such as melting, degassing, ladling and pouring]. The addition point of the grain refiner can be considered in the same terms as in DC casting. Whereas fade is not really an issue for launder additions in the casthouse, it is of relevance in the foundry, where additions are typically made to a ladle which may be left for several hours prior to use.

IV. Overview of the use of Different Refiners

A summary of the use of grain refiners in the wrought sector is presented here:

4.1 Twin roll casters:
Low boron refiners are often used (the dense TiB2 particles tending to settle particularly at the relatively slow metal flow rates encountered in this process). End applications can often be surface critical and low boron refiners can also be of benefit compared to the 1%B containing refiners. The Al-Ti-C system may also provide benefits in this process in terms of less particle agglomeration, reduced chemical segregation, as well as finer grain sizes at the higher casting speeds.

***4.2 Electrical conductor applications*:**
Al-5%Ti-1%B and Al-3%Ti-1%B are used. If too much boron is added at boron treatment, it can be almost impossible to grain refine. The Al-Ti-C system seems to suffer less from this issue and is finding increasing usage, as significant reductions in addition rate as well as improvements to product quality can be achievable.

***4.3 Extrusion billets (mostly 6xxx alloys)*:**
For the DC casting process Al-5%Ti-1%B is mainly used as the principle requirement is refiner potency. Some Al-3%Ti 1%B is also used. In terms of avoiding the formation of columnar crystals, Al-5%Ti-1%B provides the best robustness in terms of temperature sensitivity [3]. A feature of the Al-Ti-C system is consistency of grain size across the billet section [4], and possibly an improved surface finish on extrusion (the refiner particles being one potential cause of die lines, or streaking on anodising).

4.4 Rolling slabs:
Subsequent to DC casting these are processed to a variety of end applications, which can affect the refiner chosen, as discussed in the following:

4.4.1 1xxx slab:
The refiner used is dependent on the end application, as highlighted in the previous sections, but a number of 1xxx alloys fall into the category of surface critical.

4.4.2 2xxx slab:
The main refiners used are Al-5%Ti-1%B and Al-3%Ti-1%B.

4.4.3 3xxx slab:
The main refiners used are Al-5%Ti-1%B and Al-3%Ti-1%B. The Al-Ti-C refiners are generally not used as there is thought to be a mild poisoning effect with Mn.

4.4.4 4xxx slab:
The main refiners used are Al-5%Ti-1%B and Al-3%Ti-1%B.

4.4.5 5xxx slab:
The Al-Ti-B system dominates, but there is increasing usage of Al-Ti-C due to no negative effects on Mg oxide build up [5]. The Al-Ti-C system also has benefits in terms of less chemical segregation.

4.4.6 6xxx slab:
The main refiners used are Al-5%Ti-1%B and Al-3%Ti-1%B (see also comments above on extrusion billets).

4.4.7 7xxx slab:
The Al-Ti-C system is finding most of its use in these alloys, particularly the Zr containing ones due to the poisoning effect with the Al-Ti-B refiners.

4.4.8 8xxx slab:
The refiner used is dependent on the end application, as highlighted in the previous sections.

4.5 Foundry sector:
This sector is dominated by Al-5%Ti-1%B, however, growth is seen with substoichiometric refiners (such as TiBloy) particularly in wheel foundries, where reduced levels of rejects are being experienced. The foundry sector consists of foundry ingot producers (who are generally in the wrought sector), large foundries (where master alloy grain refiners dominate) and very many small foundries (where both master alloy refiners and salts/tablets refiners are used). Combined modifier (Sr) and grain refiner (Ti, B) master alloys (such as Strobloy) are also used.

V. SUMMARY AND CONCLUSIONS.

Grain refinement of aluminium and its alloys has become common industrial practice. The immense technological importance of this field has led to extensive investigations by many industrial and academic researchers during the past 60 years. A great majority of the past investigations were primarily focused on the search for grain refiners that act quickly and provide the grain refining effects without fading even on prolonged holding of the molten alloy. Among a number of grain refiners developed, Al–5Ti–1B master alloys are more popular due to their high grain refining efficiency with respect to many aluminium alloys. Al–Ti–C master alloys are also becoming popular as grain refiners for many aluminium alloys, particularly when boron is not desirable in the aluminium alloy.

The grain refining behaviour of the master alloy appears to be sensitive to its microstructure, particularly the morphology and size distribution of $TiAl_3$ particles, which are in turn influenced by the processing parameters used in the preparation of the master alloy, such as reaction temperature, reaction time, and thermo mechanical treatment

Much work has been focused on attempts to understand the mechanisms of grain refinement and several theories have been proposed. However, none of these theories can explain all the observations made in the grain refining experiments. Perhaps more than one mechanism operates depending on the grain refiner used, the alloy being cast, and the casting process involved. Further work is necessary in this direction to develop a unified description of grain refinement, poisoning, and fading.

References

[1] N.Towsey et al.*"Impact of grain refiner addition on ceramic foam filter performance"*, International Congress: Continuous Casting, DGM, (2000), 26-32

[2] G. Mabry et al. *"Characterisation of particulate captured by a rigid tube filter"*, TMS Light Metals, (1997), 983-989

[3] W.Schneider and P.S.Cooper *"Influence of AlTiB master alloy type and casting conditions on grain refinement of aluminium alloys"*, 8th Australian Asian Pacific Conference, (2003), In press

[4] W.Schneider et al.*"A comparison of the behaviours of AlTiB and AlTiC grain refiners"*, TMS Light Metals, (1998), 953-989

[5] A. J. Whitehead et al.*"Development of a commercial Al-3Ti-0.15C grain refining master alloy"*, TMS Light Metals, (1996).