THE EFFECTIVENESS OF A GRAIN REFINER REINFORCED BY A BUILT-IN ENERGY CONTENT

M. Vader and J. Noordegraaf
Kawecki-Billiton Metaalindustrie B.V.
Kloosterlaan 2, 9936 TE Delfzijl, The Netherlands

Abstract

Nucleating particles should contain enough built-in energy to form, above the T liquides, a stable germ on which solidification can start. The cooling rate and alloy composition can largely influence this phenomena. Melt agitation via electromagnetic or ultrasonic energy input can influence a homogeneous start in the outer skin of the cast. However, in order to continue the original fine grain, the presence of active particles in the melt is essential. The dotation of these particles to the melt in an optimally effective form and the exclusion of any harmful side effects, is an advantage that the new generation of grain refiners offers. The theory behind the nucleation defines the particles needed. Optimal grain refining is achieved via Statistical Process Control (SPC) and special production methods.

Introduction

When solidifying Aluminium, a driving force is needed for the nucleation and growth of the Aluminium crystals. This driving force can be an undercooling or a super-saturation. It is necessary to guide the solidification of Aluminium in order to obtain a equiaxed and homogeneous structure. Normally, this is controlled by the addition of AlTiB grain refiner. The different mechanisms from which the nucleation is obtained are largely dependent on the equilibrium conditions which exist after grain refiner addition. The peritectic "Hulk" theory first presented at the Light Metals Conference 1989 (see Ref. 1.), which explained the nucleation and growth phenomena of Aluminium, has been further validated by extensive modelling efforts and experiments carried out by Prof. L. Bäckerud (see Ref. 2, part I and II). The rate determining steps have been studied in depth and a summary of the outcome of this study is given below. The theory relates to 10 stages, which bear an important effect on overall grain refiner performance. A schematic summary of these steps is given in the appendix.

The Aluminium melt

(Step 1.)

Most commercial Aluminium metal, even in virgin condition, contains trace elements such as Silicon and Boron in substantial quantities. All melts contain a degree of Titanium, originating from Bauxite and/or recycling. Upon addition, the master alloy Aluminium melts and its effectivity is influenced by these trace quantities.

$TiB_2/TiAl_3$ dissolution

(Step 2.)

Following the addition of an AlTiB based grain refiner, the Al_3Ti and TiB_2 components are introduced into the melt. An important factor is that, after this dilution step, the solubility of the Titanium and Boron will define the possible creation of the nucleating particles. Another important factor is that the dissolution of both Ti and some of the Boron will always be accomplished under the prevailing conditions.

Diffusion of Titanium and Boron in the Aluminium melt

(Step 3.)

Research into the solubility of Titanium and Boron in an Aluminium melt was carried out by Finch et al (see Ref. 3.). These results have not been significantly altered in more recent publications (see Ref. 4 and 5.). The outcome of the literature supports the theory that a fraction of the Boron added goes into solution at a level of a tenth of

Light Metals 1990
Edited by Christian M. Bickert
The Minerals, Metals & Materials Society, 1990

ppm's. Thermodynamic calculations (see Ref. 2,part II) have shown that the Boron concentrations reach a saturation level within seconds when sub-micron size borides are added, emphasizing the importance of small boride particles in a master alloy.
The Al_3Ti phases will also dissolve. Calculations (see Ref. 2, part II) show that naked Aluminides (<100 μm.) can be dissolved within 3 to 10 seconds, providing there are no other limitations.

Coverage of Al_3Ti phases (mending)
(Step 4.)

When Aluminides dissolve a positive concentration of Ti gradient into Aluminium is created which, with the presence of Boron in solution, forces TiB_2 to reprecipitate conform the local solubility product. The Aluminide dissolution rate competes with the TiB_2 precipitation and determines the rate of TiB_2 coverage on the same Aluminide. This process may lead to a total TiB_2 coverage blocking of the Titanium dissolution. A determining factor for this step is the original TiB_2 particle size.
Mandatory for an effective coverage are; a small TiB_2 particle size and, preferably, the presence of will dispersed TiB_2 particles in the Aluminide, which is a direct outcome of the master alloy production process.
It is assumed that a small quantity of coarse borides (tail size) is a direct measure of the entire boride distribution size at sub-micron level. Due to the fact that the detection limit of the extraction method is 1.4 μm., only particles in excess of this amount can be quantified. By relating the amount of particles to the boride content in the master alloy, a utility rate can be calculated as a function of the Ti/B ratio.

Table I. Number of TiB_2 particles per unit volume for various master alloys related to the amount of Boron, can be used to calculate a utilization rate for Boron

	N_{TiB_2} >1.4 μm. per unit volume (thousands)	%B	N_{TiB_2}/%B	Relative N_{TiB_2}/%B compared to 5/1	Utilization B content
5/1	2000	1	2000	1	1
3/1	3000	1	3000	1.5	0.6
5/0.2	250	0.2	1250	0.53	1.87
5/0.05 IntoPal 0.05–0.1%B	20	0.05	400	0.20	5

It appears that the utility rate increases rapidly while the Boron content decreases, which implies that the low Boron content AlTiB alloys become relatively more effective. The optimal Ti/B ratio being between 50/1 and 100/1.
A conclusion to be drawn from Table I and Fig. 1. is that; with a low Boron content a very effective grain refiner with an extremely fine boride size can be produced

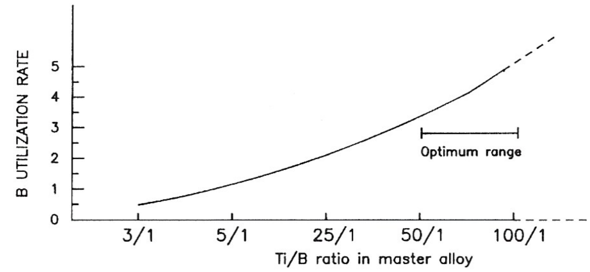


Fig. 1. Utilization rate of B as a measure of grain refiner effectivity in AlTiB commercial master alloy.

Completed peritectic cell
(Step 5.)

The Aluminide, now covered by TiB_2, will mend itself continuously as long as sufficient Titanium is present, as a possible release of Ti will give rise to local precipitation of TiB_2 due to the local solubility product.

The peritectic "Hulk" (Ti flux through TiB_2 layer)
(Step 6.)

Calculations by Prof. L. Bäckerud show that even an extremely thin layer of TiB_2 (of 65 Å) on Al_3Ti spheres can effectively prevent an Aluminide from dissolving (see Ref. 2, part II).

Boride layer thickness cm.	Dissolution time sec.	Fraction of TiB_2 used
$6.1 \; 10^{-5}$	$8.5 \; 10^{8}$	100%
$6.5 \; 10^{-7}$ (65Å)	$9.1 \; 10^{6}$	1%
$6.5 \; 10^{-8}$	$9.1 \; 10^{5}$ (250 hours)	0.1%

Evidence of the survival of such an Al_3Ti has been found in Al-Cu alloy samples, to which 0.02%Ti in the form of AlTiB5/1 was added. Al_3Ti particles of 1μm., covered with TiB_2, were found in this alloy. The protective layer of TiB_2 must have been very effective otherwise the Al_3Ti would have been entirely consumed during solidification, resulting in an TiB_2 empty shell.

Formation of peritectic liquid inside the shell
(Step 7.)

It can be understood that outward diffusion of Titanium will be balanced by inward diffusion of Aluminium, leading to a formation of a Titanium enriched Aluminium liquid inside the shell with a composition of Al-0.15%Ti.

Nucleation of α-Aluminium
(Step 8.)

This so formed peritectic liquid provides an ideal nucleation site for α-Aluminium at temperatures significantly above equilibrium temperature (T_e) in accordance with classical theory.

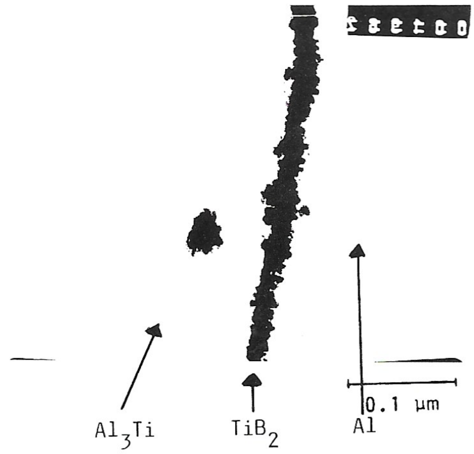
Growth of α-Aluminium
(Step 9.)

Upon the cooling of such a cell in the peritectic Al-TiO.15% liquid, α-Aluminium is formed above the bulk equilibrium temperature. This α-Aluminium is stabilized by a quantity of Titanium, originating from the Aluminide. The cell is consumed during the peritectic transformation. The actual cooling rate determines the survival rate of these nucleating sites. The size of the peritectic cells follow a normal distribution with an average size of 5-10µm. The largest cells can survive even very low cooling rates, during which the small cells are depleted. High cooling rates can also lead to survival of smaller cells, yielding a fine grain size when high cooling rates are employed.

The solidified product
(Step 10.)

Under normal conditions all peritectic cells are consumed and only the boride cover remains in the grain centre. The presence of these cells can only be demonstrated by looking at artefacts. Evidence of this phenomena can be obtained on lab scale by rapid quenching of a solidifying melt (see Fig. 2).

Fig. 2. Evidence of sub-micron TiB_2 coverage on a 10µm. Al_3 Ti lead to full coverage of the Aluminide.



Implication for selection of grain refiner

The selection of a grain refiner is governed by 4 factors, the constitutuinal effect, the particle size distribution, the tendency to form hulks and its overall versatility.

Constitutional effects

The physical requirements for a grain refined structure are schematically indicated by Fig. 3. Nucleation takes place above the equilibrium temperature (T_e) of the alloy. The growth of the grains, provided that the number of nuclei is sufficient, can only take place below the equilibrium temperature. The growth undercooling, defined as the difference between T_e and T_g determines the growth of equiaxed dendrites in the melt. This parameter is a balance between the heat generated from the release of latent heat and the heat extracted during solidification.

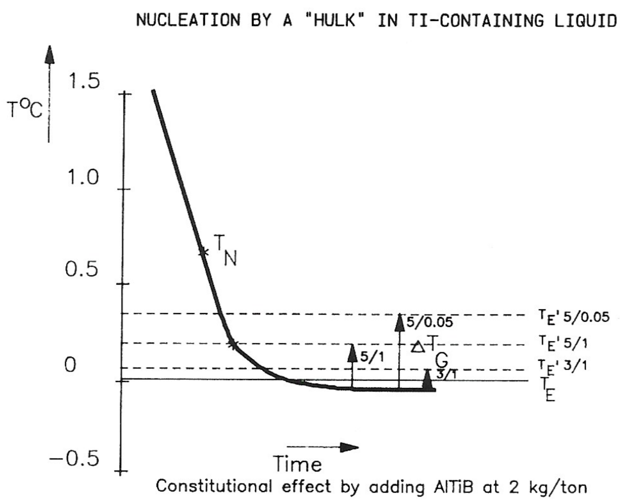


Fig. 3.

This constitutional effect is very dependent on the type of alloy and the accumulation of alloying elements. The re-distribution of solute as determined by the Sheill equation is calculated to allow for undercooling. The AA alloys 2000, 3000 and 5000 generate a high undercooling, whereas the low alloyed 1000 and 6000 series generate a significantly lower undercooling. A fact worthy of note is that the constitutional effect can be obtained either with high constitutional undercooling due to alloying elements, or by adding elements which raise the equilibrium temperature. Titanium is very effective in this respect. The effect of an addition of dissolved 0.005%Ti is equal to an equilibrium rise in temperature of almost 0.2°C., as has been calculated in Ref. 2, part II.

Table II.

Master alloy type	Free Ti as Al_3Ti	Max. % Ti Liquid in solution at 2 kg/ton addition	Additional growth undercooling
5/1	2.80	$53\ 10^{-4}$	0.17°C
3/1	0.80	$4\ 10^{-4}$	0.04°C
5/0.2	4.56	$91\ 10^{-4}$	0.30°C
5/0.05 IntoPal 0.05–0.1%B	4.89	$92\ 10^{-4}$	0.31°C

Particle size

The Percentage of Boron in the master alloy binds a quantity of Titanium in the ratio 2.2/1 (Ti/B). The various Ti to B ratio's available on the market must give rise to differing qualities of free Ti (unbound to TiB_2).

5/1 and 5/0.2 discharge a lot of constitutional Titanium, whereas the other ratio's such as 3/1 discharge very little (see Table II.). It is, therefore, easy to understand why 3/1 is a restricted choice and why 5/0.2 and 5/1 are far more competent to grain refine both pure Aluminium and alloys. With the highest percentage of Boron, 5/1 offers both a significant constitutional effect and a significant quantity of TiB_2 particles. The general trend is depicted in Fig. 4. The stoichiometric range of Ti to B, which forms the intermetallic compounds TiB_2, is 2.2/1.

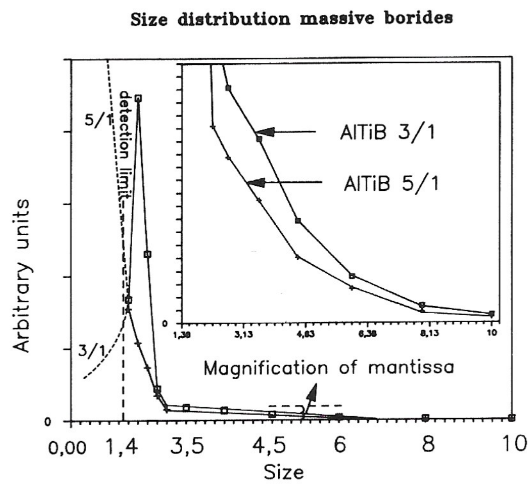


Fig. 4.

Of all commercial AlTiB alloys the 3/1 ratio seems to be the closest to this ratio. It can be understood that, from minor variations in the Ti/B ratio during the metal-salt reaction in AlTiB production, the fluctuations will reach a statistically closer proximity to 2.2/1 in AlTiB 3/1 than in any other Ti/B ratio (see Fig. 5.).

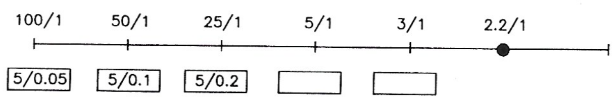


Fig. 5. Ti/B ratio in several commercial AlTiB master alloys related to the stoichiometric TiB_2 ratio.

As a result, the abundance of unwanted TiB_2 clusters and agglomerates in 3/1 alloys as well as the TiB_2 particle size of single particles is significantly higher in 3/1 than in the other Ti/B ratio alloys, namely 5/1 and 5/0.2. This side effect in particular, in conjunction with overall effectivity, has led major aluminium companies to abandon the 3/1 ratio in favour of 5/1.

Peritectic "Hulk" formation

As the dissolution of Al_3Ti is extremely rapid, only the smallest TiB_2 particles will go into solution to contribute actively to the mending process. The master alloy, therefore, with the finest boride size distribution can be expected to be the one which yields the highest quantity of hulks.

Versatility

A summary of all aspects which lead to the selection of the optimal grain refiner is given in Table III. The 5/1 ratio can be utilized because of its properties in pure and alloyed Aluminium. The 3/1 is finding application in highly alloyed products with a high percentage of scrap content only (residual Titanium). The low Boron product is mainly applicable in critical low alloyed applications, such as foil and litho sheet application. The effectivity of a given Ti/B ratio in several Aluminium alloys has previously been reported (see Ref. 7.) and results demonstrated that the 5/1 ratio is more effective than 3/1.

Table III.

Ti/B ratio	Constitutional effect	Fineness of particle size	Hulk forming ability	General versatility	All–in appraisal	Application trend
5/1	++	+++	+++	+++	excellent	increasing in bulk and critical application
3/1	+	++	++	++	good	diminishing in favour of 5/1
5/0.2	+++	++++	+	+	good	stable in critical application
5/0.05 IntoPal 0.05–0.1%B	+++	++++	+	+	good	increasing in critical application

The case for CREM

The development of electromagnetic stirring during solidification CREM has received a lot of attention (see Ref. 6.). One item worthy of note appeared to be that the grain refiners could be eliminated.
To obtain fine equiaxed grains, however, growth centres are mandatory and are added most effectively by the use of AlTiB rod. As reported by Pechiney, the need for grain refiner addition could be adjusted but not eliminated entirely. This offers substantial scope for the application of low Boron AlTiB grain refiner.

Quality Assurance

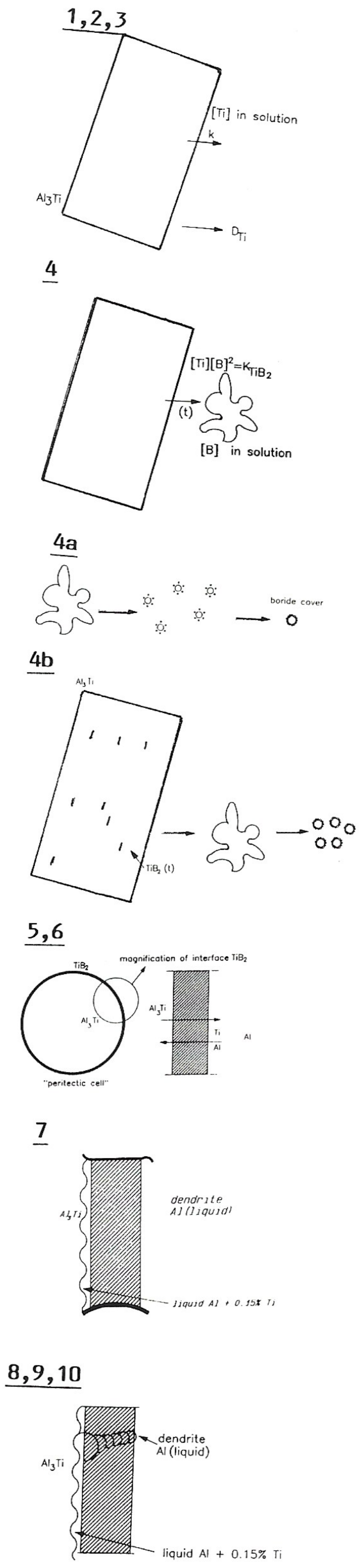
The stringent requirements of large Aluminium producing companies are, nowadays, based on requirements beyond quality control. This lead KBM to initiate a major effort in this area and become, as a result, the worlds first master alloy producer to gain an approval on the ISO 9001/BS 5750 part I quality standard granted by Lloyd's Register of Quality Assurance, certificate no. 881452, on the 6th of July 1989. This is the highest level attainable and includes items such as development, design, manufacturing and marketing and is applicable to rod, ingot, piglet and splatter production.

References

1. The New Approach To Grain Refining. M. Vader and J. Noordegraaf. Proceedings of Light Metals Conference, Las Vegas, February 1989. Edited by P.G. Cambell, TMS 1988, pp. 937-941.
2. Grain Refining Mechanisms In Aluminium As A Result Of Additions Of Titanium And/Or Boron Part I - Nucleation And Growth Below The Bulk Liquidus Temperature. L. Bäckerud and S. Yidong. J. Inst. Met., to be published.
   Part II. - Nucleation And Growth Above The Bulk Liquidus Temperature. L. Bäckerud, P. Gustofson and M. Johnsson. J. Inst. Met., to be published.
3. N.J. Finch. Met. Trans 3, (1972), pp. 2709-2711.
4. J.L. Murray. Mrt. Trans. 19A, (1988), pp. 243-247.
5. Thermodynamic Calculation Of The Al-Rich Corner Of The Al-Ti-B System. Z. Metallkunde 80, (1989), pp. 361-365. F.H. Hayer et al.
6. First Experience Of Commercial Operation With The CREM Process. G. Hidault et al. Proceedings of Light Metal Conference, Las Vegas, February 1989.

Edited by P.G. Cambell, TMS 1988, pp. 769-775.

7. Interrelations Between Aluminium Grain Refining By Means Of Aluminium Titanium Boron Alloys And The Number Of Growth Centres. M. Vader and J. Noordegraaf. Paper presented at the 8th International Leichmetalltagung, Leoben, Austria, 21st-25th June 1987, pp. 464-467.



1. a) Aluminium matrix liquifies

2. a) Dissolution of small $(Ti,Al)B_2$ particles ruled by the ternary phase diagram (5,6), yielding [B] in solution.

3. a) Diffusion of Ti into the melt (D_{Ti}).
   b) Simultaneously, diffusion of B into the melt (D_B).

4. a) Further dissolution of pure Al_3Ti while becoming covered with a TiB_2-like passivation layer with a thickness of several nanometers called "encapasulation", giving e.g. 1 nucleus out of each aluminide.

4. b) Simultaneously, dissolution of duplex type of Al_3Ti i.e. Al_3Ti containing passivation elements (8) called "mending", giving e.g. 5 nuclei per aluminide.

5. Formation of peritectic cells completed.

6. Titanium flux and aluminium counter flux through the passivation layer.

7. Creation of a layer of Titanium-rich liquid aluminium with composition in accordance with the binary AlTi phase diagram.

8. As temperature falls, nucleation of α-Al starts in this liquid in the cell; The Peritectic Hulk.

9. Formation of dendrites with subsequent piercing of the passivation layer.

10. Growth of α-Al, controlled by the peritectic transformation

Appendix 1.: Visualization of the Peritectic Hulk theory.