Managing Grain Refining Efficiency: The Way Forward for Aluminum Casthouses

By Dr. Rein Vainik. MQP

Editor's Note: Aluminum has come to the fore especially in transportation industries as one of the most efficient materials, resulting in aluminum casthouses needing to rapidly increase production of the high internal and surface quality of slab and billet to make their products. But the process of grain refinement, ensuring products are the best quality, has left a lot to be desired. Celebrating its 20th anniversary, MQP's aluminum specialist Dr. Rein Vainik discusses the challenges and pioneering work being done to take the industry forward.

Grain Refiner Overview

Grain refiners are sold to casthouses and foundries with one purpose—to create a fine-grained structure in the cast aluminum. Or that's what they should do. In principle, all aluminum melts must be grain refined to avoid cracks in the cast product. This is achieved by adding grain refiners that contain particles that act as substrates for aluminum grains when the liquid metal is solidifying.

Throughout the history of grain refiners, however, the focus has been on properties such as their chemical composition, cleanliness, aluminide particle size, and vanadium content. Virtually nothing has been published about their nucleation efficiency, namely their ability to nucleate crystals, which is ultimately the only property that really matters for a grain refiner.

Today, the most common grain refiners for aluminum and its alloys are aluminum-based alloys containing 3-5% Ti and 0.2-1% B and the active particles for nucleation are TiB_2. The most common types are 3/1 and 5/1, where the first contains 3% Ti and 1% B and the latter 5% Ti and 1% B. There are also grain refiners where the active nucleants are TiC, but these are not widely used due to their weak nucleation properties.

Grain refinement of aluminum itself was established in 1930 when it was found that a higher concentration of Ti in the melt produced smaller crystals in the cast product, and Ti was then extensively used for this purpose. In 1949, research showed that the actual nuclei in the Ti containing melts were either TiB_2 or TiC particles, present as impurities in the aluminum.[1] In the 1950s, the Al-Ti-B waffle was introduced, an ingot containing TiB_2 particles and Ti to be added to furnaces. The drawback here was that a large fraction of the TiB_2 particles, which have almost twice the density compared to liquid aluminum, sedimented in the furnaces, which meant more frequent cleaning. In the 1960s, the rod type Al-Ti-B grain refiner was developed, which allowed precise grain refiner additions in the launders leading to the casting pits.

During the process of going from grain refining with only Ti to present day grain refiners, the importance of the function of Ti was lost. Grain refinement is not only about adding nucleant particles, it is also dependent on the constitution of the alloy to be grain refined, as explained hereafter, where Ti plays a particularly important role.

Grain Refiner Efficiency Research: It was not until ten years ago that efficiency was put on the agenda. There was a need for a more precise calculation to assess the efficiency of grain refiners on the market.[2-4] The output from grain refiner tests is normally a grain size, and grain refiners are differentiated by difference in grain size at the same addition rate. MQP researchers decided to use the volume of the grains and relate that to the number of grains per volume measured metallographically to the amount of B added (Figure 1).

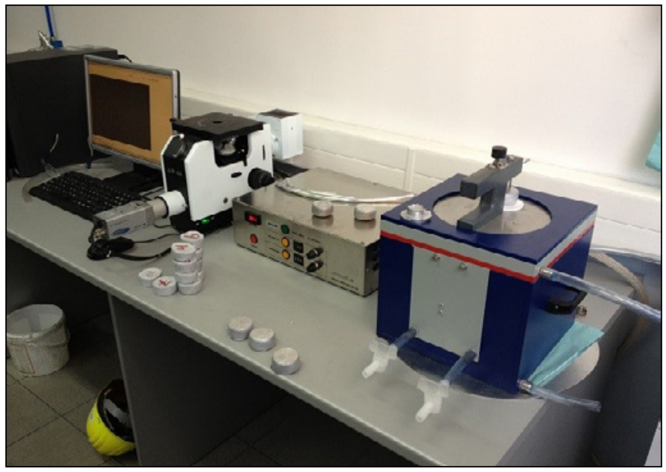

Figure 1. MQP's Opticast metallographic system (Opticube) for measuring efficiency of aluminum grain refinement whereby the sample is moved between three stations on the system for polishing, rinsing, and anodizing.

Under the supervision of Prof. A.L. Greer, researchers presented a calculation that indicated the optimal way to fill a three-dimensional space was by the tetrakaidecahedron.[5] They also derived an equation that relates the number of grains to the intercept grain size, as follows:

$$N_V \approx 0.5/L^3 \quad (1)$$

where N_V is the number of grains per unit volume and L is the line intercept value, expressed in mm, so the number of grains is given per mm^3. In the MQP definition of efficiency, this is divided by the boron concentration, expressed as ppm B, to compare grain refiners at selected addition rates, as follows:

$$\text{Efficiency} = (\text{Number of grains/mm}^3)/\text{Added ppm B} \quad (2)$$

Nucleation of Aluminum Grains on Boride Particles

Grain refinement with Al-Ti-B grain refiners is a result of nucleation of aluminum on boride particles and growth of the nucleated aluminum grains. Current research shows that the boride particle size distribution in a batch of grain refiner is considered a primary cause of differences in the nucleation performance. However, high-resolution transmission electron microscopy (HRTEM) has now also shown the presence of an Al_3Ti layer on the surface of the TiB_2 particles. This monolayer is assumed to determine whether the TiB_2 particles are potent nucleants or not, based on the work of Greer, et al.[5]

So, how does nucleation work? When a grain refined melt reaches the solidification temperature or when it reaches a temperature slightly below this temperature (i.e., it is undercooled), nucleation will occur on selected particles.

A basic principle regarding particle size is that the larger the particle, the lower the undercooling needed for nucleation. A consequence is that larger particles will nucleate first. This nucleation and initial growth of solid aluminum will raise the temperature in the solidifying melt to its solidification temperature, at which point it will remain until all aluminum has solidified.

This rise in temperature will effectively stop any nucleation and growth on smaller particles, meaning that the grains formed originally will fill up the entire solidified volume, thus define the grain size. There are two ways to measure particle size distribution: measurement in situ by SEM (i.e., the grain refiner itself) or measurement after dissolution of the rest of the material in acid or other media.

Figure 2 shows the microstructure in a cross section of an Optifine grain refiner (developed by MQP), prepared parallel to the rod direction. Aside from the aluminum matrix, two particle species are seen here—the rectangular Al_3Ti particles and the much smaller boride particles often present in larger agglomerates, in which the particles seem to be attached to each other. The matrix and Al_3Ti particles dissolve rapidly when the grain refiner is added to liquid aluminum, while the boride particles are dispersed into the liquid metal.

Figure 2. Microstructure in Optifine, 3% Ti/1% B grain refiner; two areas with elongated boride agglomerates are marked with circles.

The question is begged, when measured in the cross section, how large a fraction of the measured particles will still sit together when the grain refiner is added to the melt and will the particles collected after acid dissolution really reflect the situation in a melt? Measurement of the particle size distribution in a grain refiner by Greer, et al.,[5] can be seen in Figure 3, where the total number of boride particles was estimated to be about $5x10^4$ per mm^3 and the small black bars represent the particles they considered to be active as nuclei, i.e., particles that have a diameter over 3 µm.

The way grain refiners are tested at MQP is to investigate the fraction of particles that will nucleate aluminum grains under the prevailing conditions, i.e., the cooling rate and growth restriction induced by base Ti concentration in the melt. This can be said to be a direct way to measure the fraction of active particles—without the limitations other methods suffer from.

Growth Restriction: The curtailing of growth of the early nucleated grains, growth restriction, is one of the key mechanisms to understanding grain refinement. The curves in Figure 4 show results from three different lab scale experiments. Three melts, based on a 99.7 pure Al, were prepared with different Ti concentrations. Each point represents a sample of the melt, into which a grain refiner sample was added, the proportion given by the addition rate axis. The same grain refiner batch was used for each sample. The microstructures for the samples indicated with red and green squares in Figure 4 are shown in Figure 5. Note that the number of boride particles added is the same in both samples, since the addition rate is about equal, but there is a large difference in grain size. The reason for this is the growth restriction effect.

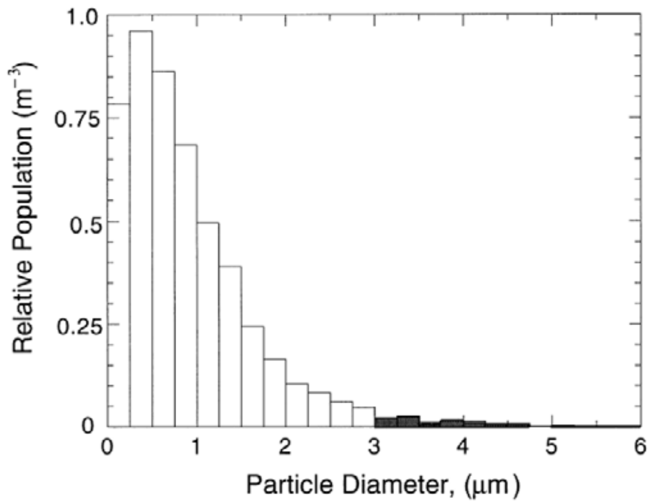

Figure 3. Particle size distribution in an 5/1 grain refiner as determined from image analysis of scanning electron microscope (SEM) micrographs.

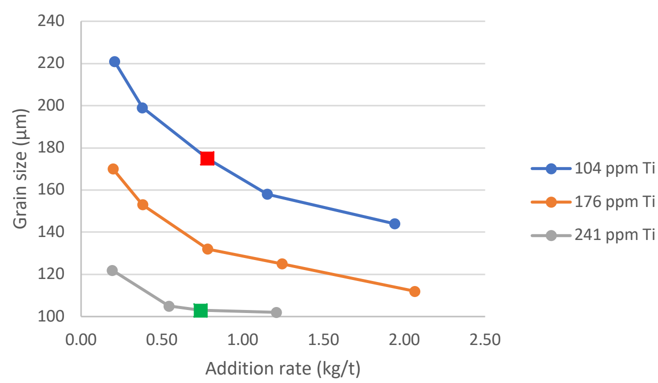

Figure 4. Results from three different lab scale experiments on the effect of Ti concentration in 99.7% aluminum on grain size for a constant grain refiner addition

All samples shown in Figure 4 have been cooled at the same rate, so in this case, it is the composition of the melt that governs the growth rate, i.e., the difference in Ti composition. The presence of Ti in liquid aluminum has a dramatic influence on the growth rate and this interaction between aluminum and Ti is unique compared to all other elements used for alloying aluminum.

Figure 5 shows that grain size decreased from 175 to 104 µm at an addition rate of about 0.75 kg/t just by increasing the Ti from 104 to 241 ppm, i.e., 0.0104 to 0.0241%. The reason is that Ti reduces the growth rate of new grains, allowing more nuclei to be active as sites for aluminum grains. This is possible because, during solidification, the temperature is essentially constant due to the evolution of solidification heat. An efficiency calculation on the samples shown in Figure 5 is presented here. For a sample containing 104 ppm Ti (0.78 kg/t, 175 µm), the calculation is as follows:

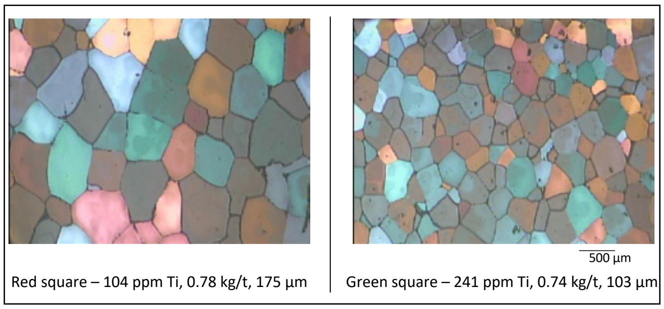

Figure 5. Microstructures for the samples indicated with red and green squares in Figure 4 are shown.

$N_V \approx 0.5/0.175^3 = 93$(Grains/mm^3)
Efficiency = 93/7.8 ≈ 12(Grains/mm^3·ppm B)

For a sample containing 241 ppm Ti (0.74 kg/t, 103 µm), the calculation is as follows:

$N_V = 0.5/0.103^3 = 458$(grains/mm^3)
Efficiency = 458/7.4 ≈ 62(grains mm^3·ppm B)

By increasing the Ti concentration from 104 to 241 ppm, the efficiency ratio of 62/12 shows that the same amount of boride particles nucleate 5.2 times more aluminum grains in the sample containing 241 ppm Ti compared with the 104 ppm containing sample.

The aluminum rich corner of the Al-Ti phase diagram is shown in Figure 6. Two important features on the phase diagram are points A and B. A is the peritectic point defined by 0.15% Ti and 665°C. Point B is defined by 1.35% Ti and 665°C. However, the most important features are m, representing the slope of the liquidus curve, and k, representing the partition coefficient. These parameters of the phase diagram define the growth restriction in a system, denoted Q:

$$\text{Growth restriction} = Q \approx m|k-1|C \quad (3)$$

in which, C is the concentration of the element. In an alloy with different alloying elements, the Q factors are added and contribute to growth restriction:

$$Q \approx \sum m|k-1|C \quad (4)$$

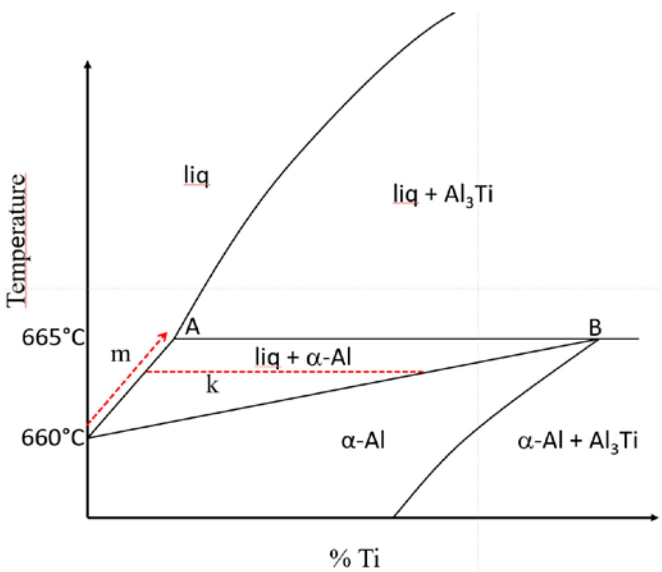

Figure 6. Al rich corner of the Al-Ti phase diagram.

The growth speed of dendrites is inversely proportional to the growth restriction factor:

$$\text{Dendrite growth rate} \propto 1/Q \quad (5)$$

This means that increased concentrations of elements will decrease the growth rate of dendrites and thereby contribute to a smaller grain size in the cast. Table I reveals why Ti has such a large impact on the grain size of aluminum alloy castings.

Element	k	m	$m\|k-1\|$
Ti	9	30.7	245
Si	0.14	-7.1	6.1
Mg	0.51	-6.2	3.0
Fe	0.02	-3	2.9
Cu	0.17	-3.4	2.8
Zn	0.4	-1.6	1.0
Mn	0.94	-1.6	0.1

Table I. Comparison of growth restriction factors for Ti and typical alloying elements in aluminum.

Testing Grain Refinement

There are several ways to test the nucleation ability of grain refiners including the Alcan TP-1, Alcoa, Reynolds, and the KBM ring test. All tests are valid if they manage to reproduce test results. The Opticast test was developed by MQP more than 20 years ago in close cooperation with a casthouse and the grain sizes obtained were correlated to slabs measuring 400 x 1,200 mm, in which the grain sizes were measured at about two thirds of the distance from the surface. The test sample size is about 100 g and the cooling rate is 1.5°C/sec.

MQP's experience with other methods is that they can deliver reasonable results, provided multiple samples are made and outliers are removed. The Opticast test was chosen because it more closely represents critical casting conditions in casthouses in terms of grain refiner addition rates and cooling rates and is highly reproducible.

During development of Opticast, it was vital to include reference samples in every melt prepared for grain refinement tests. This enabled the results from different melts to be compared, since all measurements are related to the same reference. Every Optifine test heat comprises 4.5 kg of Al and 16-22 samples are collected from this. Four reference samples are included in each melt to monitor if there is a change in the melt. The relative standard deviations of the efficiency values for these four samples from ten consecutive heats are presented in Table II. A 10% standard deviation is acceptable and, if the value is exceeded, the test is repeated. Two of the tests in Table II were repeated.

Heat 1	8.5
Heat 2	5
Heat 3	6.9
Heat 4	4.5
Heat 5	2.6
Heat 6	5.4
Heat 7	12.8
Heat 8	4.5
Heat 9	10.8
Heat 10	7.9
Average	**6.9**

Table II. Standard deviations for Opticast grain refining efficiency measured from four reference samples on ten aluminum heats.

The TP-1 test is a standard method for grain refiner producers. The TP-1 values are not reported for every batch, which means that there are a lot of grain refiner batches delivered without any test value that can give a hint about their ability to nucleate aluminum grains. At one time, the Aluminum Association initiated a round robin test with 12 laboratories to determine the variation in the TP-1 test. The same base metal and batch of grain refiner was sent to the laboratories and there was a substantial spread in the results.

In 2012, the Association published their report and concluded: "Grain refining is not an exact process. The base alloy, the additive, the actions in the liquid metal and the freezing metal, the variation in specimen surface preparations, and the visual acuity of operators all have important influences on the reported results of a TP-1 test. To reduce the inherent error arising from these influences, the use of the average result of multiple tests and the consideration of the standard deviation of the pooled data are recommended."[6]

Despite the shortcomings of the TP-1 test, it may be applicable to DC-casting of billets, but is not suitable for tests of grain refiners used for casting at lower cooling rates, i.e., the end results may be a too large grain size in the cast. Instead, a method with a slow cooling rate will differentiate low and high efficiency grain refiners in a better way and the result from such a test is applicable to any cooling rate.

The TP-1 and Opticast tests were compared, showing that the relative efficiency difference between two grain refiners will remain similar regardless of the test used. However, to be certain about the actual TP-1 test value, multiple samples must be made.

Grain Refiner Tests: Optifine is a grain refiner containing 3% Ti and 1% B. It has the same chemical composition and structure as any other grain refiner with this composition. It can directly replace any other 3/1 grain refiner in any type of casting application. In fact, it can replace any type of grain refiner that contains Ti and B, if the necessary growth restriction is adjusted by addition of Ti.

The difference between Optifine and other grain refiners is that it exhibits a consistent, high efficiency, having up to ten times the number of active nuclei when compared to the worst performing batches of standard grain refiners, enabling addition rates to be reduced sometimes by over 70%. Every batch is tested using the Opticast test to ensure a minimum relative efficiency is met.

Figure 7 shows results of the grain refining tests performed on ten standard grain refiner samples that were collected and tested against Optifine during casting of an AA6060 alloy. Efficiencies were calculated for the best of the standard grain refiners (no. 7) and for three of the low efficiency grain refiners (1, 9, and 10). The results are shown in Figure 8 and summarized in Table III.

The last column in Table III (Factor) contains values produced by dividing the Optifine efficiency with the efficiency for respective batch. As an example, it shows that for no. 10, the least efficient of the standard grain refiners, 4.7 times more is needed compared to Optifine when the addition is about 0.2 kg/t. At 0.45 kg/t, 6.9 times more is needed.

Ultimately, particle size measurements by the standard LIMCA method have provided evidence that Optifine can reduce the number of particles >20 μm in the liquid metal by up to 70% compared with standard Al-Ti-B grain refiners. Together with this potential improvement in quality, a facility casting 300,000 tpy and purchasing 300 tons of standard grain refiner at a typical average cost of $1.17 million could reduce its costs by 50% over a range of compositions, a saving of $585,000.

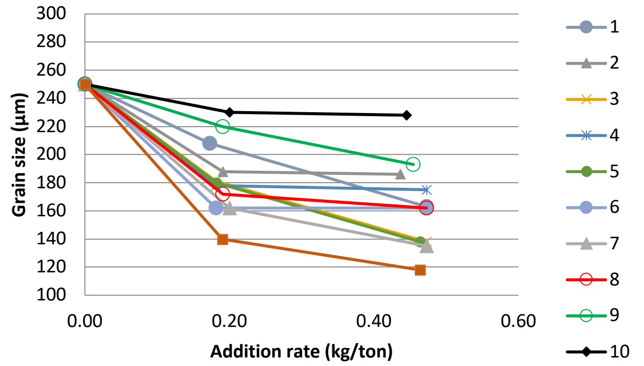

Figure 7. Opticast test on various standard grain refiners from a casthouse store.

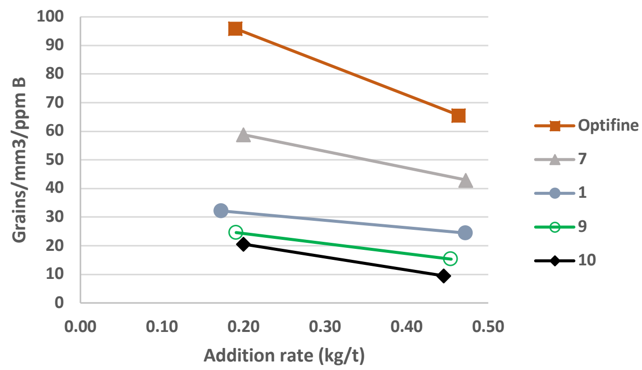

Figure 8. Efficiency values for selected grain refiner batches from Figure 7.

Sample	Addition Rate (kg/t)	Grain Size (µm)	Efficiency (Grains/ mm^3/ppm B)	Factor
7	0.20	162	59	1.6
1	0.17	208	32	3.0
9	0.19	220	25	3.9
10	0.20	230	21	4.7
Optifine	0.19	140	96	—
7	0.47	135	43	1.5
1	0.47	163	24	2.7
9	0.45	193	15	4.3
10	0.45	228	9	6.9
Optifine	0.46	118	66	—

Table III. Comparative test results for various grain refiner samples against Optifine in the casting of an AA6060 alloy.

Casthouse Testing of Various Grain Refiners

~~Between six to 15 grain refiner batches were collected from casthouse stores and samples weighed to give addition rates, relevant for the alloys to be tested. The first test was a screening test, with the aim of comparing the efficiencies of the standard grain refiners against Optifine.~~ Figure 9 shows the screening test results made at a billet casthouse. The test was performed in an AA6060 melt with 12 standard grain refiner batches and the standard addition rate of 0.75 kg/t was applied.

Of 12 batches of grain refiners, none was found to have a higher efficiency than Optifine, defined by the 100% line, but several got close. Since the standard addition rates were relatively high at this casthouse, they managed the casts without problem. An exception was number 10.

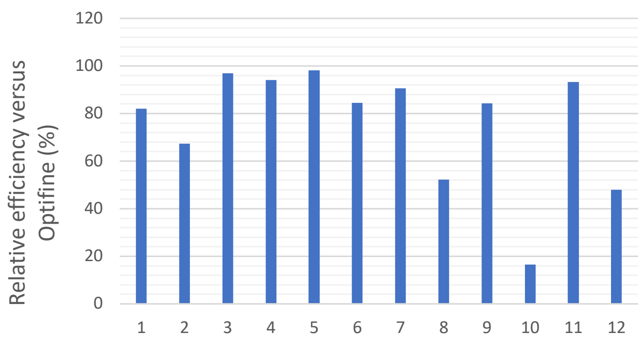

Figure 9. Screening test at billet casthouse in an AA6060 melt with 12 standard grain refiner batches at a standard addition rate of 0.75 kg/t applied.

This batch had not yet been used in the casthouse and was scrapped because of the investigation.

After the screening test, Opticast samples were taken during casts of alloys to be optimized, while standard grain refiners were used to grain refine the cast. Figure 10 shows the grain refinement curves produced during a cast of AA6060. Grain refiner no. 12 showed less than 50% efficiency compared to Optifine. The average grain size at the standard addition rate of 0.7 kg/t for grain refiner no. 12 (163 µm) can be obtained at an Optifine addition of 0.16 kg/t—a reduction of 77%. However, a full reduction should not be directly implemented, but taken step by step.

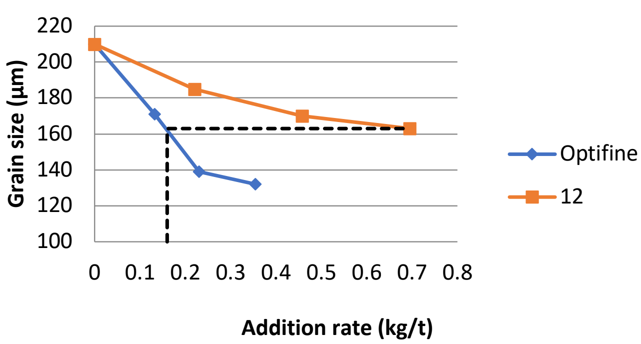

Figure 10. Shows the grain refinement curves for Optifine and grain refiner no. 12, produced during a cast of AA6060.

Addressing Al-Ti-C and Zirconium Poisoning

It is known that, if Zr is present in aluminum melts at concentrations over 0.05%, it affects the nucleation of aluminum grains on boride particles. Optifine is not an exception, being of the same chemistry as any other Al-Ti-B grain refiner.

Over the years, MQP has performed many tests with high Zr alloys, mainly AA7xxxx series alloys. Optifine has been tested against both other Al-Ti-B alloys and Al-Ti-C alloys and the experience is that it always achieves a finer grain size than Al-Ti-C alloys and is more efficient than other Al-Ti-B grain refiners.

Al-Ti-C grain refiners suffer from a similar spread in efficiencies than most Al-Ti-B grain refiners, but on a different level. The efficiency is lower, meaning the grain sizes are higher. Due to their low efficiency, the Al-Ti-C grain refiners are added at high addition rates, well over 2 kg/t in most cases.

A lab experiment with Optifine and Al-Ti-C grain refiner batches from two producers, A and B was performed. This test was requested by a casthouse, who also delivered the grain refiner samples and melt samples. The melt contained 0.11% Zr and the holding time for each sample was six minutes before it was allowed to solidify. The standard addition rate at the specific casthouse was 3 kg/t of Al-Ti-C. As can be seen, Optifine performed markedly better and there was also a difference between the set of Al-Ti-C batches from producer A and B.

Another experiment is shown in Figure 11, in which the Zr concentration was 0.11% and three sets of samples were made with increasing Ti concentration and tested for average grain size. It is obvious that Ti has a positive effect on the nucleation on boride particles. Whether this is due to reactions on the boride particle surfaces or whether it is due to the increased growth restriction imposed by increasing concentration of Ti, needs to be investigated.

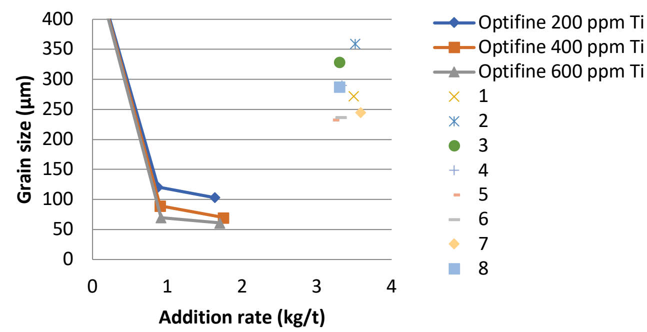

Figure 11. Another experiment where the Zr concentration was 0.11% and three sets of Optifine samples were made with increasing Ti concentration (comparison made with other grain refiners).

New Research at BCAST

A key finding by Greer, et al., was that, in order for nucleation to occur on TiB_2, a layer of Al_3Ti needed to form on the basal plane of the TiB_2 crystals.[5] On the back of this, BCAST at Brunel University continued research into the nature of the Al_3Ti layer by applying HRTEM. MQP, together with its parent company, STNM, has now entered into a two-year research program with BCAST with the following objectives:

- To reveal the characteristic of TiB_2 particles in grain refiners with different refinement efficiency and find the relationship between TiB_2 particles and the refinement efficiency
- To understand why the grain refinement efficiency of a refiner varies from batch to batch
- To enable MQP to consistently produce Optifine grain refiner batches with high efficiency

Already, it has been shown that the Al_3Ti layer is a monoatomic layer (Figure 12). The monoatomic Al_3Ti layer can clearly be seen in Figure 13. A second important discovery has been the mechanism by which the presence of Zr leads to "fading" or the loss of potency with a TiB_2 grain refiner (Figure 14).

In parallel with studies on the nature of the Al_3Ti layer, the TiB_2 size distribution and morphology will be investigated by scanning electron microscopy (SEM). MQP is excited about this project and we expect that further important discoveries will be made that will advance our fundamental knowledge of the mechanism of grain refinement of aluminum.

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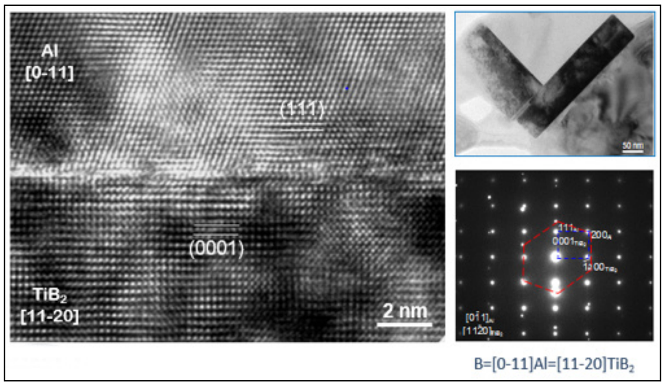

Figure 12. High-resolution transmission electron microscopy (HRTEM) conducted at BCAST of a 5:1 TiB grain refiner showing that the Al_3Ti layer is a monoatomic layer on the TiB_2 particle. (Source: BCAST.)

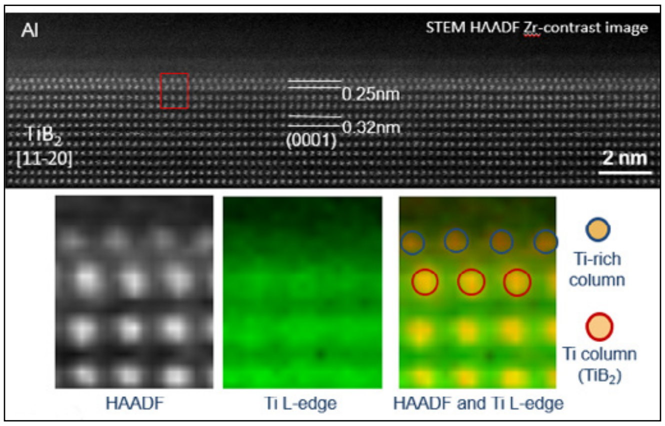

Figure 13. The monoatomic Al_3Ti layer can clearly be seen. (Source: BCAST.)

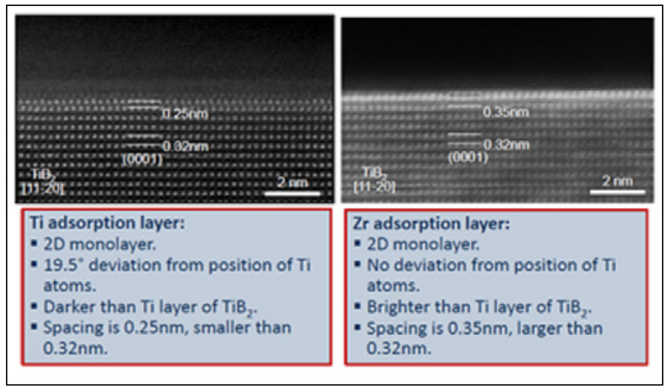

Figure 14. The presence of Zr leads to "fading" or the loss of potency with a TiB_2 grain refiner by replacing the Al_3Ti layer. (Source: BCAST.)

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