Grain Refinement of Aluminum Casting Alloys

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ABSTRACT

An overview is given of grain refinement in aluminum casting alloys. The mechanisms involved and the benefits of refinement are described. The review shows that current practices were developed long before modern Al-Ti-B refiners became available, and are employed now largely for historical reasons. The results of tests in Al-Si, Al-Si-Cu, Al-Cu, Al-Mg and Al-Zn-Mg alloys are presented. The grain refining response is different for each alloy system. It is important to understand that titanium can be present in two forms. One dissolves in aluminum; the other is nearly insoluble. Each must be controlled separately. With today's powerful Al-Ti-B refiners, there is no reason for large additions of soluble titanium in most alloys. In fact, it is better to say we grain refine with boron, not titanium. The recommended addition is 10-20 ppm of boron, preferably in the form of Al-5Ti-1B or Al-3Ti-1B rod. Lower dissolved titanium levels provide better grain refinement and an improved resistance to hot cracking in some alloys.   Al-Si casting alloys which contain copper are an exception. In alloys such as 319 or 355, it is best to have a minimum of about 0.1 % Ti.

INTRODUCTION

The grain refinement of aluminum was first accomplished by making titanium additions to the melt (Pacz, Suhr, Nock and Rosenhain, 1930-1934). The improvement in castability was considerable, and this quickly became the established practice. The resulting change in the structure of the casting is remarkable. This is may be seen by cutting a piece from the casting, and polishing the cut surface with a series of progressively finer sandpapers, until a mirror-smooth surface is obtained. After the polished surface is etched with acid the underlying microstructure is revealed. An example of the transformation obtained by grain refinement is shown in Figure 1.
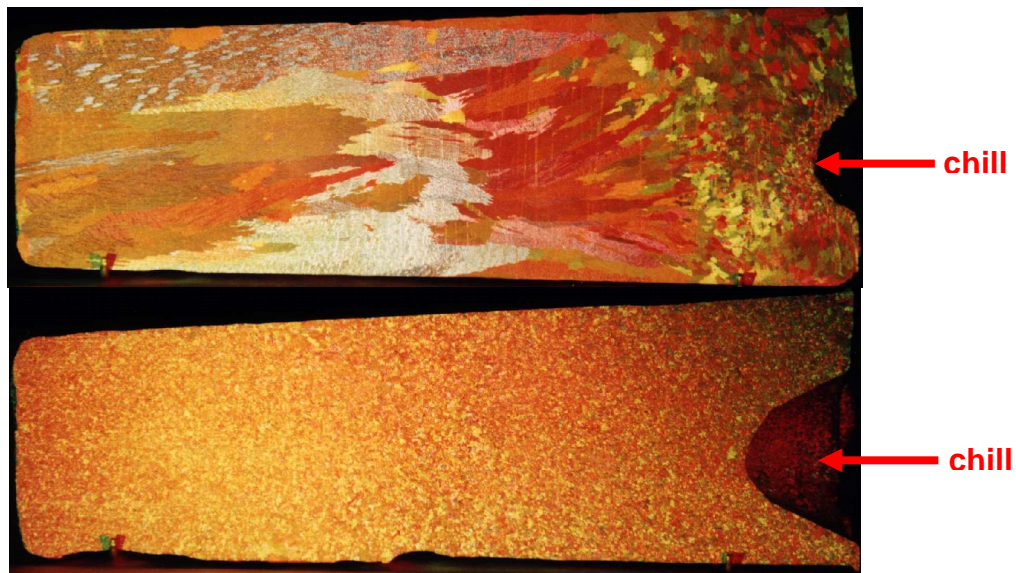
Figure 1.   Grain structure in 3004 alloy castings
(top: no refinement, bottom: 10 ppm B added as 5Ti-1B alloy)

Grain refinement has a significant effect on the mechanical properties of castings, primarily because the distribution of second phase materials is changed. Consider the casting shown in Figure 1. Looking at the non-refined casting at the top one sees a small area near the chill where equiaxed grains were formed, but the rest of the metal has elongated, 'feathery' grains. All brittle intermetallic phases and any porosity formed will be located between these large grains, so the elongation normal to the grains will be poor. The material at the bottom has a much better structure. The grain size is small (or fine, which is the basis for the term 'refinement'). Hence, mechanical properties are isotropic and the material is stronger.

As we shall see below, grain refinement in casting alloys tends to reduce the amount of porosity and the size of the pores. This improves mechanical properties, especially fatigue strength. Feeding is also improved. It is for these reasons that most cast aluminum is grain refined.

MEASUREMENT OF GRAIN SIZE

To determine grain size one obtains a sample and produces a smooth surface on one side. This may be done in the laboratory using standard metallographic techniques. However, another procedure is more convenient with large samples; for example, when cutting through the middle of a casting. The sample is placed on a milling machine, and metal is milled away until a flat surface is obtained. Then, if a final light cut *with a sharp tool* is made, the resulting surface may be etched directly without polishing.

For aluminum alloys low in copper, the test sample is placed in hot, nearly boiling water for a few minutes. Once the sample is hot, it is removed from the water and the surface to be etched is immersed briefly in a solution of Poulton's etch. (This etchant contains the following ingredients: 60% HCL, 30% HNO_3, 5% HF, and 5% H_2O.) This acid is held at room temperature. Alternatively, you may etch the surface by wiping it with a piece of cotton wool or absorbent cloth, which has been soaked in the etchant.

For alloys that contain copper, it is more difficult to determine the grain size. One procedure that works reasonably well is to etch the sample at room temperature in a solution of 10% HF. This results in a black smudge on the sample produced by the copper in the alloy. This smudge may be cleaned off by rubbing the surface of the sample under running water, or by rinsing it in a dilute solution of nitric acid.

There are various procedures established to measure grain size on the etched samples. These are outlined in ASTM E112. The grain structure can be reported in one of several units:

- -average intercept distance
- -calculated average grain diameter
- -ASTM grain size number, and
- -grains per unit area

Table 1 gives values for different units of measurement, for the sake of comparison. The easiest procedure is usually to measure the average intercept distance (AID). All grain sizes in this document are reported in this way. The units employed are microns (μm or 10^{-6} meters).

Table 1. Comparison of Various Grain Size Measurements (ASTM E112)

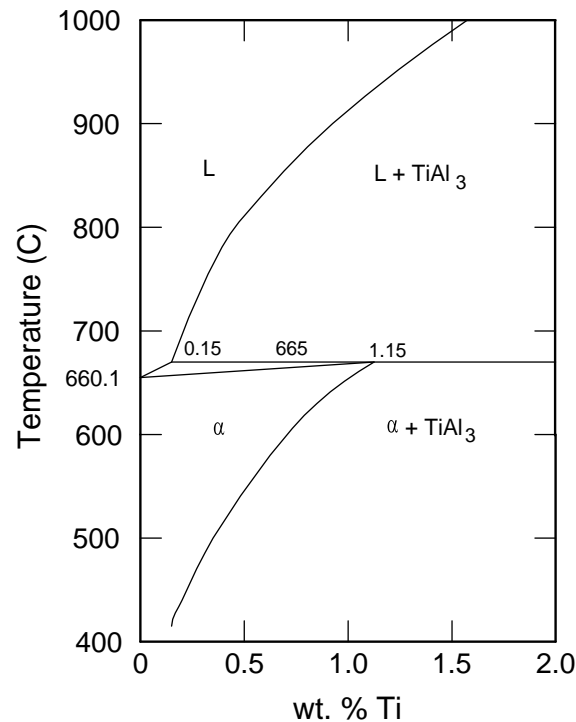| Average Intercept Distance			Average	ASTM		
inches	mm	microns	Diameter (μm)	grain No.	grains/cm^2	grains/in^2
0.008	0.2	200	252	14.5	1890	12,200
0.015	0.4	400	504	12.5	496	3,200
0.031	0.8	800	1008	10.5	112	724
0.047	1.2	1200	1512	9.5	56	362
0.079	2.0	2000	2520	8	20	128

Fig. 2. The aluminum rich side of the Al-Ti phase diagram (Sigworth, 1984)

MECHANISMS OF GRAIN REFINEMENT

Grain refinement dates from the early 1930s, when foundrymen began to use titanium additions to improve the structure of their castings. To understand this action of titanium we first consider the Al-Ti phase diagram (Sigworth, 1984), shown in Figure 2. The important thing to note is that titanium raises the melting point of aluminum: Pure aluminum melts at 660.1°C; adding Ti increases the melting point to 665 °C. This effect has important ramifications for the nucleation and growth of solid aluminum grains.

The best explanation was given in 1983 by Backerud.   Figure 3 is taken from his paper and shows schematically what happens. Titanium additions are made via aluminum master alloys, which contain between five and ten percent of titanium. These materials contain numerous crystals of the titanium aluminide compound, $TiAl_3$. (Pictures of aluminide crystals are given by Guzowski et al., 1987) When a master alloy is added, typically a few minutes before casting, millions of these microscopic particles are released into the melt. The presence of one is indicated by (1) in Figure 3. When the $TiAl_3$ crystal comes in contact with liquid aluminum, it starts to dissolve. This means the liquid metal at the surface of the particle becomes enriched in titanium, as shown by (2) in Figure 3. From the relationships shown in the Al-Ti phase diagram, the Ti-rich metal in contact with the aluminide can begin to solidify at a temperature which is *above* the melting point of the base alloy. Hence the first nucleation (or formation) of solid aluminum will be at the surface of the aluminide particle, as shown by (3). The aluminum crystal then grows around the surface of the aluminide (4 and 5). In the process it consumes the Ti in the vicinity of the particle, and growth stops. As the metal cools further, dendritic growth begins (6) and continues (7) as solidification proceeds.

This course of events may be confirmed in two ways. The first is to pour a sample of metal into a small cup, and record the temperature during solidification with a thermocouple. The resulting cooling curves of refined and non-refined metal are shown in Figure 4. When Ti is added, the nucleation temperature, Tn is often above the growth temperature, Tg. When no Ti is present, the metal cools several degrees below the growth temperature before nucleation occurs.

Another confirmation of the mechanism proposed in Figure 3 may be found by a careful examination of the microstructure of aluminum castings. When anodized in the proper way and viewed under polarized light, the Ti-rich areas corresponding to (6) and (7) of Figure 3 are revealed. An example is presented in Figure 5 (Easton and StJohn, 2000). The dark areas located in the center of the grains were shown by microprobe measurements to be high in Ti.

The above is a clear explanation of how Ti acts to grain refine aluminum, but there is an additional factor that must be considered: the dissolution of $TiAl_3$ particles. A normal addition level of Ti is around 100 ppm (0.01 %Ti). When this amount of Ti is added to relatively pure aluminum at normal casting temperatures, it dissolves. And once the added particles have dissolved, the grain refining effect disappears. This loss of refining ability with time is called 'fade'.

The fade time depends on a number of factors. The most important are the Ti content of the metal, the metal temperature, and the type of master alloy used. The latter determines the $TiAl_3$ particle size. Al-Ti rod products tend to have smaller particles and dissolve faster—typically in 10-15 minutes. Waffle products are cast from a higher temperature and have larger aluminide particles. These take 30-40 minutes to dissolve. The practical consequence in the foundry is relatively simple: If the Ti in the metal is less than the solubility (0.15% Ti at 665 ^{o}C), then it is not possible to grain refine consistently. Results from three early studies of grain refinement in high purity aluminum are shown in Figure 6 (Cole *et al.*, 1972). The best refinement was obtained when the Ti added was more than 0.15%, the solubility limit of $TiAl_3$ in aluminum.
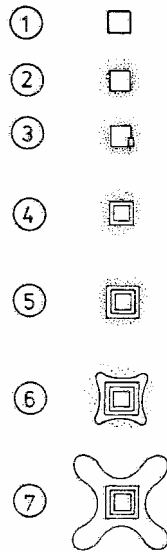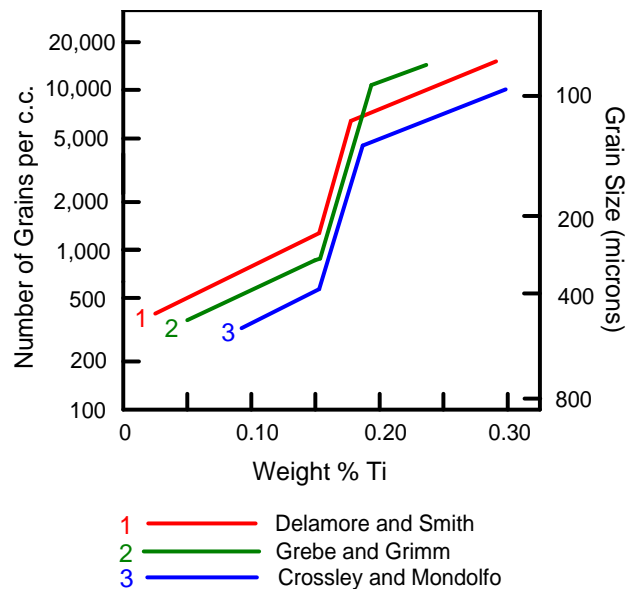

Figure 3. **TiAl₃ nucleates aluminum grain**
(after Backerud, 1983)
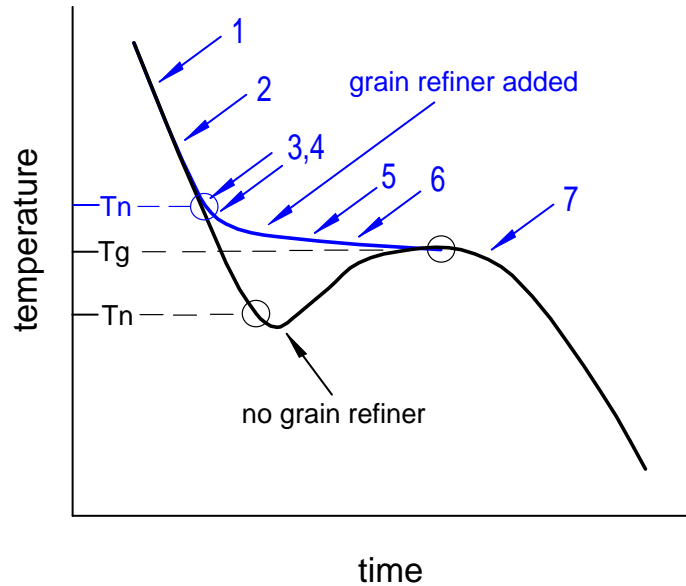
Figure 4. **Cooling curves during solidification**
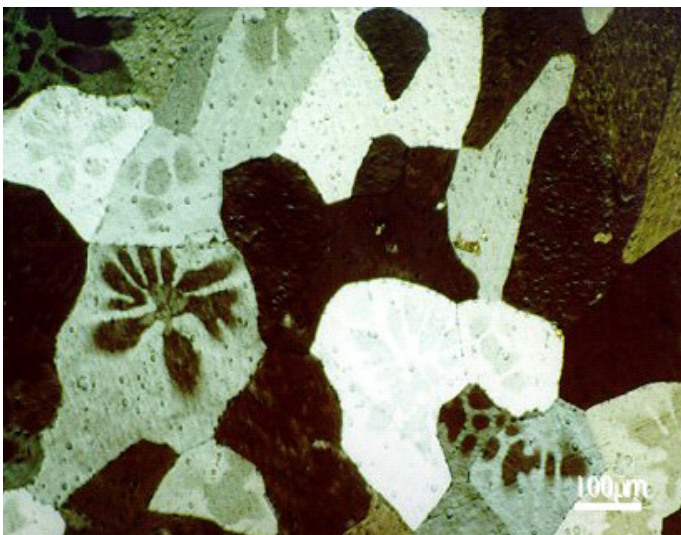
Fig. 5. Ti-rich areas in dendrites of Al-0.06%Ti alloy
(reproduced from Easton and StJohn, 2000)

Fig. 6. Refinement of 99.7% Al by titanium
(reproduced from Cole et al., 1972)

The picture we have painted so far is fairly attractive and relatively easy to understand. This understanding of grain refinement has been in our picture gallery for a long time: since 1930. During that time it has entered deeply into the consciousness of foundrymen, much like Michelangelo's *Mona Lisa* has entered the main stream of consciousness forming our popular culture. For this reason, we need to understand it well. This picture is essentially the source of, and basis for, most of the grain refinement practices used today in aluminum casting alloys.

The maximum limits for Ti are quite high in most alloys, and in some cases a minimum is specified. Take 201 alloy, for example. It is vital to grain refine this alloy to prevent hot cracking during casting. The specification for 201 alloy published by the Aluminum Association permits up to 0.35% Ti; and a minimum of 0.15% Ti is called for. Many of the other 2xx and 7xx casting alloys also have a minimum specified (0.10 or 0.15% Ti). And with a few exceptions, aluminum casting alloys permit a maximum of at least 0.20 % Ti. The reason for these large quantities of titanium might as well be engraved in stone. And as we shall see below, it should be a tombstone. In other words, the epitaph for this 75 year old grain refining practice should read:

> *"High Quantities of Ti are Necessary to Prevent Dissolution of Al-Ti Refiners"*

From an historical point of view, the above accurately describes the first 40 years of aluminum grain refinement. Then, in the early 1970s, the first modern Al-Ti-B grain refiners became available. The role of boron was studied in the laboratory as early as 1951. This work showed that boron in combination with Ti gave much better grain refinement, but the use of boron-containing salts in the casthouse was an extremely messy and haphazard business. Finally, in the late 1960s Kawecki discovered how to produce boron-containing master alloys by reacting a mixture of KBF_4 and K_2TiF_6 with molten aluminum. The result was the first commercial Al-Ti-B master alloy—a fast acting rod product that could fed continuously into the metal transfer launder or holding furnace by wire feeders. The new B-containing grain refiners were much more powerful and economical. They therefore replaced the use of the earlier Al-Ti products in most aluminum alloys; and they still form the basis for accepted commercial practices to this day.

How do the modern refiners differ from the old ones? There are many differences, but for our purposes the most important is this: Most of the Ti in modern Tibor® refiners is present as TiB_2 particles, and titanium diboride is virtually insoluble in molten aluminum. The consequence:

> *"High Quantities of Ti are NOT Necessary to Prevent Dissolution of Al-Ti-B Grain Refiners"*

But that is only part of the story. In addition to low solubility, borides are extremely effective nuclei in foundry alloys. In fact, boron is a better than titanium as a grain refiner for aluminum casting alloys.

BORON AS A GRAIN REFINER

In 1981 Lu, Wang and Kung published a study of the grain refining of A356 alloy in the Journal of the Chinese Foundrymen's Association. The results shown in Figure 7 are taken from their study. Three different master alloys were added to A356 alloy: Al-5%Ti, Al-5%Ti-1%B, and Al-4%B. The results clearly showed that boron is more powerful than titanium as a grain refiner.

This result ran completely counter to the prevailing viewpoint of the time. Everyone believed that titanium was needed for grain refinement, but the Chinese study showed that titanium was only a weak grain refiner. It also suggested that boron is much better than titanium.

Intrigued by these results, Sigworth and Guzowski (1985) began their own study. Laboratory tests confirmed that aluminum-boron master alloys containing AlB_2 particles gave excellent grain refinement. They then went to Stahl Specialty Company in Missouri, where foundry trials confirmed that Al-B master alloys were good refiners. However, the added boron reacted with dissolved titanium to produce a 'sludge' in holding furnaces. Also, boron apparently reacts with strontium, since boron additions resulted in a loss of modification in some heats modified with strontium.

This presented an interesting problem. If one compares the nucleation potency and other characteristics of the different crystals in Al-7%Si alloys, one finds:

1. $TiAl_3$ crystals are poor nuclei. $TiAl_3$ crystals also have a relatively high solubility in aluminum. For both reasons a large amount of titanium must be added to produce consistently small grain sizes.
2. TiB_2 particles are excellent nuclei. Titanium diboride has almost no solubility in liquid aluminum. Thus, TiB_2 particles produce good refinement at small addition levels. The refinement is also long lasting, when the particles are not allowed to sediment from the melt.

3. AlB_2 is the best nucleus. It produces the smallest grain size. However, AlB_2 dissolves readily in aluminum, where it reacts with titanium and strontium in the melt. Long term use produces undesirable 'sludge' in furnaces. Thus, in spite of its potency as a grain refining nucleant, AlB_2 cannot be used in the foundry.
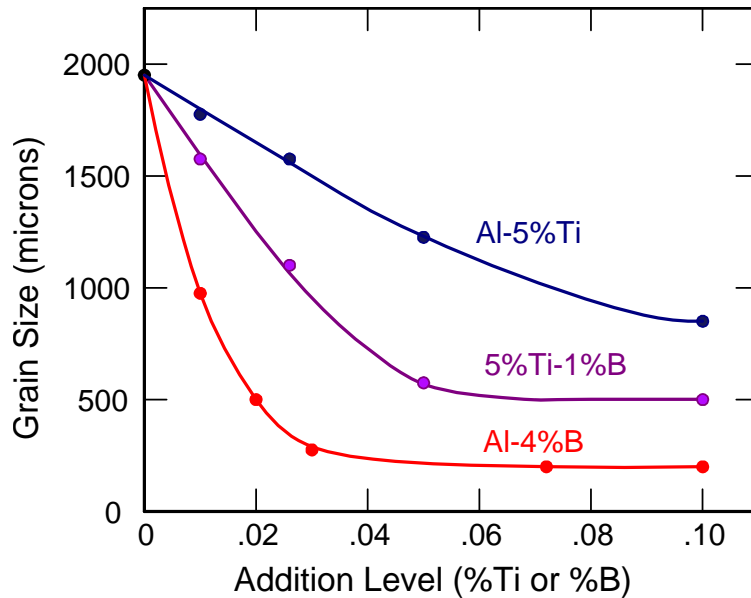

Fig. 7.   Grain refining of A356 alloy by three master alloys (reproduced from Lu, Wang and Kung, 1981)

Would it be possible to develop a grain refiner with the potency of AlB_2 and without the problems associated with boron additions? After reflecting on this question for some time, Sigworth and Guzowski produced grain refiners containing a 'mixed boride'. AlB_2 and TiB_2 have the same crystal structure and x-ray studies showed the two crystals form a continuous solid solution. Thus, a 'mixed boride' has a composition intermediate between AlB_2 and TiB_2 and can be represented by the formula $(Al,Ti)B_2$. Mixed borides appear to have a nucleation potency close to AlB_2 with a low solubility, similar to TiB_2. Thus, the problems associated with straight boron additions were avoided.

The first 'mixed boride' refiner was an Al-2.5Ti-2.5B alloys. More recently it has been produced as an Al-1.7%Ti-1.4% master alloy, marketed under the name 'Tibloy'. This is an excellent refiner, but somewhat slow acting—requiring about 5 minutes to produce the best grain size. In 356 alloy its performance does not usually justify the additional cost, but in 319 alloy 'Tibloy' refines significantly better than Al-5Ti-1B. (See Figures 17 and 18 of the 1985 paper by Sigworth and Guzowski.)

One could summarize the above discussion by saying:

"Boron is the Most Powerful Grain Refiner in Aluminum Casting Alloys"

With this understanding it is now possible to define an optimized grain refining practice for each of the common casting alloys.

BEST PRACTICES FOR GRAIN REFINEMENT

Before defining the best grain refinement practices, it is necessary to clearly distinguish between the two forms of titanium:

1. SOLUBLE TITANIUM
This is the $TiAl_3$ compound, which is present as 10-20 micron sized particles in Al-Ti master alloys which do not contain boron. It is also present in Al-Ti-B alloys which have an excess of Ti required to produce TiB_2. (The stochiometric ratio is 2.22 wt % Ti for each 1 wt % B.) The $TiAl_3$ compound dissolves quickly in alloys that contain less than about 0.15% Ti. As noted above, this particle is a poor refiner in Al-Si casting alloys.

2. INSOLUBLE TITANIUM

This is the titanium present as TiB_2. TiB_2 has such a low solubility in aluminum, that for all practical purposes it can be considered to be insoluble. (TiC is another form of insoluble titanium. The carbide is also a good grain refiner, but as it offers no advantage in casting alloys, Al-Ti-C refiners will not be considered further.)

In the past the single word 'titanium' has been used to describe both its soluble and insoluble forms. This terminology appears to be the principal reason for confusion by foundrymen when trying to understand grain refinement. Thus, to establish a linguistic foundation for an improved understanding, we propose the following terminology: The word 'titanium' shall refer to the amount of titanium dissolved in an alloy. The word 'boron' shall refer to the quantity of insoluble boride particles present.

With this terminology in mind, we can pose this question: What combination of titanium and boron gives the best grain refinement? The answer is this: It depends on the alloy family under consideration. For this reason, each is considered separately.

ALUMINUM-SILICON CASTING ALLOYS

The Al-Si and Al-Si-Mg casting alloys, such as 356 and 357, offer excellent castability and provide a range of attractive mechanical properties. Hence, they find wide spread commercial application. These alloys have also been studied extensively. The grain refining of the (copper-free) Al-Si casting alloys has been reviewed in a separate publication (Sigworth, Easton et al., 2007). The plot shown in Figure 8 is taken from this study. These results are for grain refinement of an Al-7%Si-0.35%Mg (A356) alloy. This alloy was modified with c. 0.02% Sr and grain refined with a 10 ppm B addition of Al-5Ti-1B master alloy. Castings were also poured without the boron addition. All samples were cut from a plate casting at a distance of 35mm from a chill, where the cooling rate was similar to that obtained in permanent mould cast wheels. Grain sizes were measured in accordance with ASTM E112. The average and standard deviation of the grain sizes are plotted.

It is readily seen that when TiB_2 particles are added via commercial grain refiners, the grain size of the casting is essentially constant, and independent of the dissolved Ti content in the alloy. This result was also confirmed in other experimental studies. A plot of results obtained with the Aluminum Association grain size test is given in Figure 9. Three different boron-containing grain refiners were employed. It appears a small amount of titanium (c. 0.02%) is desired when using 'Tibloy' or Al-B master alloys; but this is not necessary for TiB_2-containing refiners, such as Al-5Ti-1B.
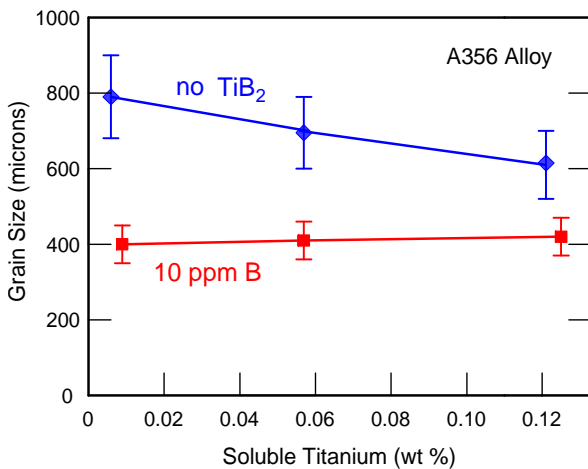
Fig. 8   Grain size as a function of Ti content
(reproduced from Sigworth, et al., 2007)
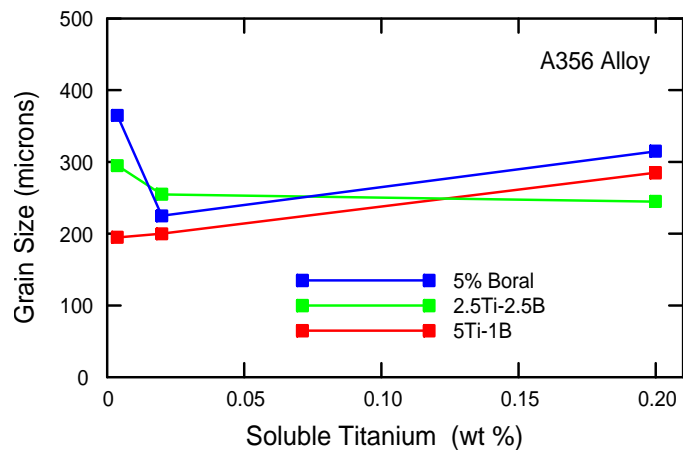
Fig. 9. A356 alloy grain size from AA test.
(reproduced from Young et al., 1991)

These results point clearly to improved grain refining practices for the Al-Si casting alloys, such as 356 and 357. Best grain refinement is obtained when 10-20 ppm of boron is added in the form of Al-5Ti-1B or Al-3Ti-1B rod. With this boron addition it is possible to reduce the large amounts of soluble Ti now added to these alloys. Lower Ti does not appear to result in any loss of mechanical properties or castability as determined by grain size. Lower Ti contents also offer the advantage that the tendency for sludge formation is eliminated. Sludge can become a significant problem when the Ti content is held over 0.10% for long periods of time. (Sokolowski and co-workers, 2000)

ALUMINUM-SILICON-COPPER CASTING ALLOYS
The grain refinement of 319 alloy was studied in detail by Pasciak and Sigworth (2001). A number of castings and solidification conditions were studied. The grain size observed in test castings, whose freezing rate was similar to that found in permanent mold castings, has been plotted in Figure 10. Both the (dissolved) titanium and (insoluble) boron contents were varied in these trials.

For some reason the presence of copper in the alloy changes completely the grain refining response to titanium. In this case it is beneficial to have a minimum of about 0.10% titanium dissolved in the alloy. Without this quantity of titanium it was not possible to produce a small grain size. The best grain size is obtained when 10-20 ppm of boron is added. The boron addition can be made in the form of Al-5Ti-1B or Al-3Ti-1B rod. A 'Tibloy' alloy can also be used, and may be cost effective; but in this case at least five minutes should be allowed for the refiner to become active.

Although they have not been studied, it is reasonable to presume that other copper-containing Al-Si casting alloys (such as 355 and 308) will behave similar to 319. For this reason, it would be advisable to have about 0.10% Ti present in these Al-Si-Cu casting alloys, before making an addition of 10-20 ppm of boron.
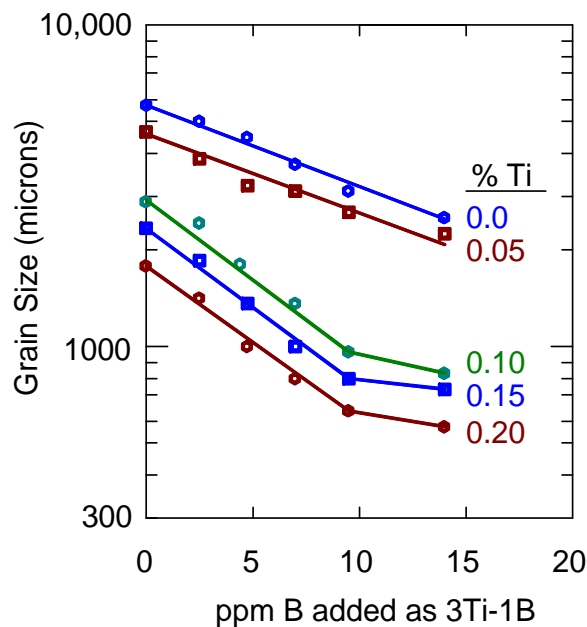

Figure 10.   Grain refinement of 319 alloy (Pasciak and Sigworth, 2001)

ALUMINUM-COPPER CASTING ALLOYS
The first casting alloy used in America was an Al-8% Cu composition, known as No. 12 alloy. In 1909 Alfred Wilm discovered that an Al-4.5%Cu-0.5%Mn alloy would strengthen, by aging after a quench from an elevated temperature. This alloy was called 'Duralumin', and formed the basis for the Al-Cu family of alloys used today. These alloys have excellent mechanical properties, high temperature strength, and fatigue life. They are difficult to cast, however. Their long freezing range makes them extremely susceptible to hot cracking.

It has long been well known that grain refinement reduces the tendency for hot cracking in net-shaped castings. The study which shows this most clearly is the 1970 paper by Davies, who found the total length of hot tears in a casting was proportional to the cast grain size. In other words, a good grain refining practice is essential for the production of crack-free 2xx alloy castings.

The specifications for 2xx alloys date from the time when titanium was used as a grain refiner. For this reason a minimum content of 0.15% Ti is specified for 201, 202, 203, 204 and 206 alloys. More recently, however, it has been shown that lowering the titanium content reduces the grain size of the casting and improves hot crack resistance. (Sigworth and DeHart, 2003) The best grain size and hot crack resistance are obtained when the titanium is less than 0.05%, and 10-20 ppm of boron is added as Al-5Ti-1B or Al-3Ti-1B rod.

ALUMINUM-ZINC-MAGNESIUM CASTING ALLOYS

A number of aluminum casting alloys are based on the ternary Al-Zn-Mg system. These alloys age naturally to high strength at room temperature. A high temperature solution and aging treatment is not required. Consequently, the 7xx casting alloys have the potential to deliver properties nearly equivalent to conventional 356-T6 (Al-Si-Mg) castings. There is a potential cost saving that can be realized by eliminating the heat treatment, especially with complex shapes that would tend to distort when quenched from a high temperature. Castings from these alloys may also be welded or brazed immediately after casting, and the assemblies will age to high strength at room temperature. This combination of properties makes the alloys promising candidates for a number of applications.

In spite of their excellent properties, the 7xx casting alloys are seldom used, mainly because of their propensity for hot cracking. As a consequence, the AA chemical composition limits established for Ti in these alloys have relatively high upper limits; and in three alloys (712, 771 and 772) a minimum Ti content (0.10 or 0.15%) is specified.

A recent study has shown that low titanium contents in these alloys reduce the grain size and improve hot crack resistance. (Sigworth, Kaufman and co-workers, 2004) The best grain size and hot crack resistance are obtained when the titanium is 0.02 to 0.05%, and 10-20 ppm of boron is added as Al-5Ti-1B or Al-3Ti-1B rod.

ALUMINUM-MAGNESIUM CASTING ALLOYS

The 5xx casting alloys provide extremely good corrosion resistance and moderate strength without heat treatment. They are commonly used in marine and architectural applications. The alloys are not easy to cast. The high Mg content produces a thick, 'sticky' oxide film on the melt, and castings are susceptible to hot cracking and shrinkage. The AA chemical composition limits established for these alloys have relatively high upper limits for Ti; and in three alloys (516, 520, and 535) a minimum content of 0.10 % Ti is specified.

Sigworth (2001) conducted a study of the grain refinement of Al-7%Mg (535) alloy. Two alloys were prepared, having the same composition except for the soluble titanium. The chemistry of the two alloys is given in Table 2.

Table 2. Composition of Al-Mg Alloys Tested

Alloy	wt.% Cr	wt.% Cu	wt.% Fe	wt.% Mg	wt.% Mn	wt.% Ni	wt.% Si	wt.% Ti	wt.% Zn
535	0.0	0.004	0.15	6.98	0.18	0.002	0.05	0.196	0.0
535L	0.0	0.004	0.15	7.04	0.18	0.002	0.05	0.036	0.0

To each alloy an addition of 30 ppm B was made in the form of Al-3%Ti-1%B master alloy. Grain size samples were taken by using the test specified by the Aluminum Association. The resulting grain size, as measured by the average intercept distance, is shown in Table 3.

Table 3. Grain Sizes Observed in 535 Alloys

Alloy	Grain Size (microns)
535	82
535L	86

Since the statistical (1σ) error associated with the determination of grain size is about 10%, for all practical purposes the two alloys have the same grain size. Thus, it appears the soluble Ti has little effect in 5xx alloys. This is result is similar to that found above for Al-Si and Al-Si-Mg alloys, such as 356 and 357. In other words, it should be possible to reduce the Ti content of Al-Mg alloys without affecting castability, when boron is used as a refiner.

BENEFITS OF GRAIN REFINEMENT

Grain refinement tends to reduce both the amount of porosity and the size of the pores in casting alloys. The reason for this may be seen by careful examination of the structure in a casting. (Figure 11) In 356 alloy the first 50 or 60 percent of the solidification process is taken up by the formation and growth of aluminum grains. Then a film of Al-Si eutectic forms around the aluminum dendrites. Gas porosity typically forms during the last five to ten percent of the solidification process. Thus, gas must fit into the spaces available between the aluminum dendrites and solidified eutectic. (The pores are seen as black areas between dendritic grains in Figure 11.) When the grain size is reduced, the size of the spaces available for pores is also reduced. The consequence is a smaller pore size.
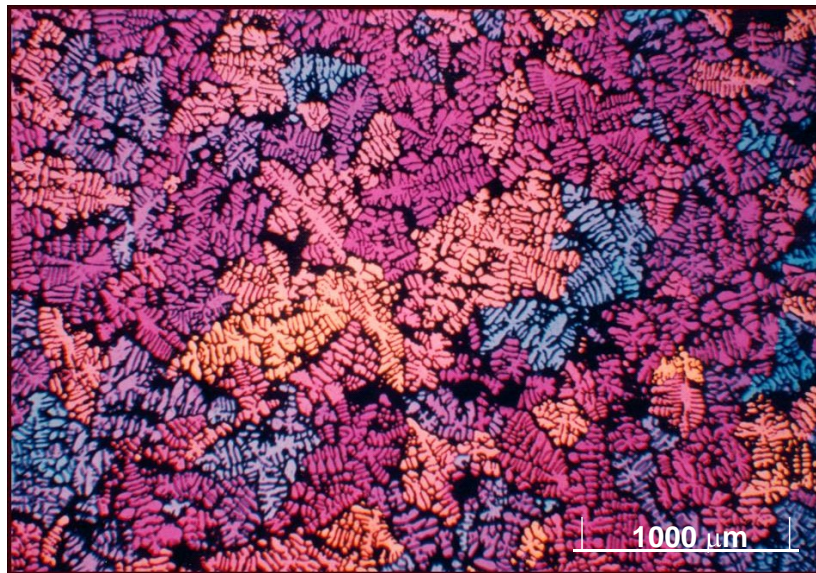
Figure 11.   Grain structure in an A356 alloy casting.

Figure 12 shows a plot of measured pore size in directionally solidified A356 alloy castings. By comparing curves (1) and (3) of this figure, one can see that grain refinement reduces the size of pores formed. (Rapid solidification also reduces pore size.) The result is an improved fatigue life for the casting.
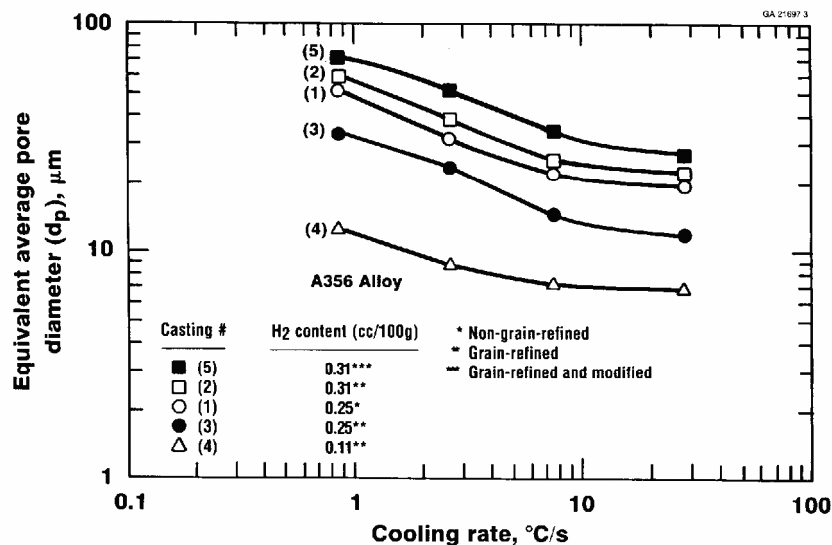

Figure 12.   Pore size in A356 alloy castings (from Fang and Granger, 1989)

The other major benefit of grain refinement is improved feeding and a reduced tendency for shrinkage formation in the casting. The mechanism for this effect was first established by Guocai Chai (1984), who placed a slowly rotating paddle in a solidifying cylindrical casting. By measuring the torque on the paddle, he was able to measure the point during solidification when the semi-solid 'mush' started to 'jell', or become stiff. This transition point he called dendrite coherency. Coherency indicates the time when solid grains start to connect with each other to reduce feeding. Chai's measurements showed that grain refiner additions delay the onset of dendrite coherence. Figure 13 presents results obtained for an Al-4%Cu alloy solidified at two different cooling rates.   Without grain refinement dendrite coherency occurs at 25% solid; with grain refinement coherency occurs at 50% solid. This means that a grain refined riser behaves like a liquid nearly twice as long as a non-refined riser. The measurements of Chai were later duplicated in other alloys by Arnberg and Backerud (1996).
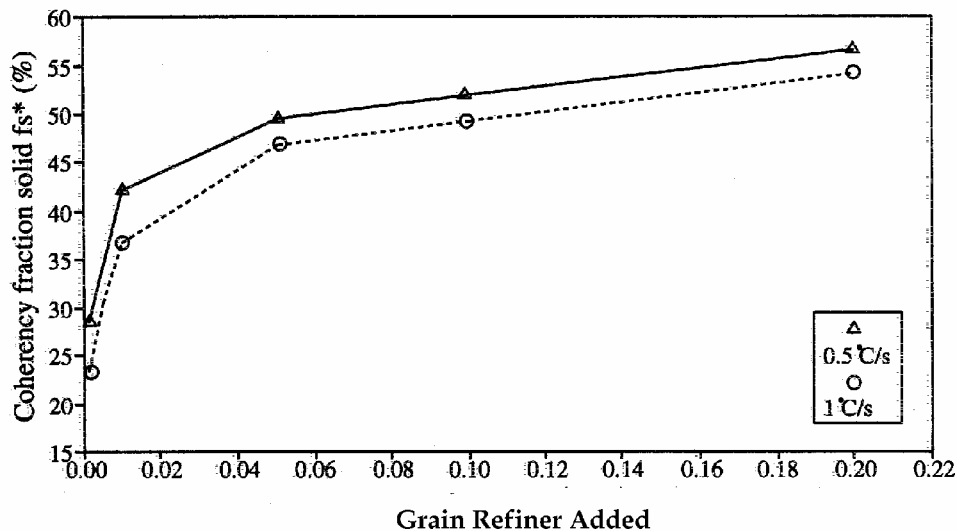
Figure 13.   Dendrite coherency in an Al-4% Cu alloy (from Chai, 1994)

CONCLUDING REMARKS

A detailed review of grain refinement in aluminum casting alloys has shown that the large titanium additions commonly used, and often specified, are primarily an historical artifact. Titanium was used by itself for nearly 40 years, and with this practice large additions are needed for good results. Now that powerful Al-Ti-B refiners are available, however, there no longer is any reason (with one exception) for large titanium additions. Lower Ti contents eliminates the tendency for sludge formation, and in some alloys a smaller grain size and improved resistance to hot cracking is found.

The first key to an improved understanding of grain refinement is to realize that titanium can be present in two different forms: as soluble and insoluble particles. The soluble form is called 'titanium' in this paper. The insoluble form is called 'boron', since insoluble titanium is present as titanium diboride. The second key is to realize that boron (boride particles) is an extremely powerful nucleant in all casting alloys. Boron is much more effective than titanium. Thus, it makes more sense to say that we grain refine with boron.

It then becomes a question of which combination of titanium and boron gives the best results. The answer depends on the alloy system. A summary is offered below:

1. LOW TITANIUM IS BEST
The Al-Cu and Al-Zn-Mg alloys give best results when the soluble titanium content is kept low, preferably less than about 0.05 % Ti. The grain size is reduced and the resistance to hot cracking is improved in most castings. This runs counter to the accepted view, since many of these alloys call for a relatively high minimum Ti level. Examples are: 201, 203, 204, 206, 240, 242, 710, 712, 713, 771, and 772.

2. TITANIUM HAS LITTLE EFFECT
In many alloys the titanium content has little effect on grain size, when a powerful boron-containing refiner is employed. The Al-Si, Al-Si-Mg and Al-Mg alloys fall into this category. Examples are: 356, 357, 358, 359, 512, 520 and 535.

3. HIGH TITANIUM IS BEST
Tests in 319 alloy have shown that it is necessary to have a minimum of about 0.1% Ti in order to produce a small grain size. By analogy, other Al-Si-Cu alloys presumably would also benefit from high titanium additions. Examples are: 308, 319, 354, and 355.

In all of the above cases the best grain refinement practice is to make an addition of 10-20 ppm of boron, preferably in the form of Al-5Ti-1B or Al-3Ti-1B rod. A 'Tibloy' alloy can also be used, and may be cost effective in hard to refine alloys (like 319), but at least five minutes must be allowed for the refiner to become active.

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