

THE EFFECT OF ALLOY CONTENT ON THE
GRAIN REFINEMENT OF ALUMINIUM ALLOYSM.A. Easton* and D.H. StJohn[†]

CRC for Cast Metals Manufacturing (CAST)

*Department of Materials Engineering, Monash University, Melbourne, Australia

[†]Department of Mining, Minerals and Materials Engineering, University of Queensland, Brisbane, AustraliaAbstract

A recent model that predicts the effect of solute content on grain size was shown to predict the effect of titanium additions on the grain size of pure aluminium and an AlSi7Mg0.3 alloy. The model assumes that nucleation on substrates is facilitated by constitutional undercooling in front of a growing grain. To determine how generally applicable the model is to a broad range of aluminium alloys, titanium additions were made to five wrought alloys containing the same level of TiB₂. It was found that the grain size obtained is a function of the reciprocal of $m_i c_0 (k-1)$, the growth restriction factor, and that there is a lower limit to the grain size that can be achieved for the casting conditions used in the experiments. It was also found that at least stoichiometric levels of titanium are required for TiB₂ particles to be effective nucleants.

Introduction

The mechanism of grain refinement by titanium-boron master alloys in aluminium alloys has been debated for over 50 years. During this time, many theories have been proposed to explain phenomena observed when grain refining additions are made to aluminium alloys. However most of the debate has been over the role of the nucleant substrate [1]. While the role of solute in reducing the grain size has been acknowledged [2, 3], close consideration has not been given to quantifying the role of solute elements in the achievement of a fine grain size. Likewise if the solute content of an alloy does have a considerable effect on the grain size achieved by addition of master alloys, then it is possible that grain refinement practice can be tailored to a particular alloy thus providing savings on grain refinement additions for casthouses.

There are two parameters that have been used to quantify the effect of solute on the grain size of a casting:

- the growth restriction factor, $m_i c_0 (k-1)$, designated Q after Greer et al. [4] (also known as GRF [5]), and

- the supercooling parameter, $\frac{m_i c_0 (k-1)}{k}$, designated P after

Spittle and Sadli [6],

where m_i is the gradient of the liquidus slope, c_0 is the concentration of the solute in a binary alloy and k is the partition coefficient. Relative values of both of these factors per unit concentration are listed in Table 1 for a range of binary aluminium based alloys. The high value of Q for titanium is thought to be why titanium reduces the grain size dramatically when added in small amounts [2].

Table I. Data required for calculating the growth restriction factor, Q, and the supercooling parameter, P, for binary aluminium alloys. The relative magnitude of Q and P of the various solutes can be compared using the data in the $m(k-1)$ and $m(k-1)/k$ columns respectively [10]. The data for Al-Ti was obtained from [2].

Element	k_i	m_i	max. conc. (wt%)	$m(k-1)$	$m(k-1)/k$
Ti	7-8	33.3	0.15	~220	~30
Ta	2.5	70	0.10	105	42
V	4.0	10.0	~0.1	30.0	7.5
Hf	2.4	8.0	~0.5	11.2	4.7
Mo	2.5	5.0	~0.1	7.5	3.0
Zr	2.5	4.5	0.11	6.8	2.7
Nb	1.5	13.3	~0.15	6.6	4.4
Si	0.11	-6.6	~12.6	5.9	53.7
Cr	2.0	3.5	~0.4	3.5	1.8
Ni	0.007	-3.3	~6	3.3	4714
Mg	0.51	-6.2	~3.4	3.0	5.9
Fe	0.02	-3.0	~1.8	2.9	145
Cu	0.17	-3.4	33.2	2.8	16.5
Mn	0.94	-1.6	1.9	0.1	0.1

The growth restriction factor was originally derived by Maxwell & Hellawell [3], from a solution [7] of the diffusion equation for the case of diffusion limited growth of a spherical precipitate. Later Hellawell [8] stated that the significance of the parameter $m_i c_0 (k-1)$ is that it is proportional to the amount of constitutional

undercooling that can be generated. However it is actually $\frac{m_i c_0 (k-1)}{k}$ or P that is equal to the amount of constitutional undercooling that can be generated [9]. As has been shown by Easton & StJohn [5], P does not explain the powerful effect of titanium solute additions for grain refinement in comparison to other elements such as silicon (see Table I for a comparison of the Q and P values for silicon and titanium in aluminium).

By assuming that solute undercooling is dominant, and by considering the growth of a dendrite tip, Hunt [11], Rappaz & Thévoz [12] and Chai [13] found that the diffusion limited growth rate of a dendrite is given by,

$$V = \frac{AD_l(\Delta T)^2}{\Gamma m_i(1-k)c_0}$$

where A is a constant, D_l is the diffusion coefficient, Γ is the Gibbs-Thomson parameter, and ΔT is the undercooling below the liquidus.

It has been suggested [13, 14] that in multi-component alloys, Q can be determined by adding the Q values for the individual solute elements. However, the validity of the additive nature of the growth restriction factor was recently tested and it was found that this method can grossly overestimate the actual value particularly for Al-Si foundry alloys [9, 15]. It was concluded that data from multi-component phase diagrams or thermodynamic packages such as Thermo-Calc® need to be used to obtain more realistic values of Q.

It has been suggested that solute decreases the grain size either by restricting the growth of grains which reduces the rate of latent heat formation thus allowing further nucleation events to occur [3] or by providing the undercooling required for nucleation to occur on available substrates in front of the growing solid-liquid interface [5].

Model for the Prediction of Grain Size

Recently a model was developed that predicts the relative change in grain size due to changes in solute content and the potency of nucleant particles present in the melt [9]. The basis of this model is an equation which relates the development of constitutional undercooling to the development of solid fraction based on Scheilian solidification, where

$$\Delta T_c = m_i c_0 \left(1 - \frac{1}{(1-f_s)^p} \right) \tag{1}$$

where f_s is the fraction solid and $p = 1-k$.

An important parameter for comparing the effect of solute on the grain size achieved is the initial rate of development of the constitutionally undercooled zone as this determines how quickly the undercooling necessary for nucleation is achieved. The initial rate of development of constitutional undercooling is defined by $\frac{d\Delta T_c}{df_s}$ at $f_s=0$.

By differentiating Equation 1,

$$\frac{d\Delta T_c}{df_s} = m_i c_0 (k-1)(1-f_s)^{k-2}$$

and at $f_s = 0$,

$$\frac{d\Delta T_c}{df_s} = m_i c_0 (k-1) \text{ which is the Growth Restriction Factor, Q.}$$

Therefore Q is a measure of how rapidly the constitutionally undercooled zone is formed at the earliest stages of growth. This factor was found to be the same for both the assumption of solidification according to the lever rule and the Scheil equation [9].

The development of constitutional undercooling with fraction solid, calculated using Equation 1, is shown in Figure 1 for AlTi0.02 and AlTi0.05. It is seen that adding titanium to pure aluminium leads to a significant increase in the rate of the development of constitutional undercooling.

In order to predict the relative grain size it is assumed that a grain must grow to a particular solid fraction, f_{sn} , to produce the constitutional undercooling equivalent to the undercooling required for nucleation of another grain on an adjacent nucleant substrate, ΔT_n . When f_{sn} is considered as a distance a grain grows before the next nucleation event occurs then f_{sn} is representative of the distance between nucleation events. The distance between nucleation events sets the grain size in the final microstructure. f_{sn} can only be regarded as a relative prediction of grain size since the relationship between f_{sn} and an actual measure of distance is not known. For the purpose of determining the effect of solute content and nucleant particle type on grain size a term, relative grain size (RGS), can be defined as being the fraction solid, f_{sn} , at which the constitutional undercooling, ΔT_c , reaches the undercooling required for nucleation, ΔT_n . Therefore, using equation 1,

$$RGS = f_{sn} = 1 - \left(\frac{m_i c_0}{m_i c_0 - \Delta T_n} \right)^{\frac{1}{p}} \tag{2}$$

The actual grain size of a casting is assumed to be proportional to the RGS. This equation can be used for any binary alloy system.

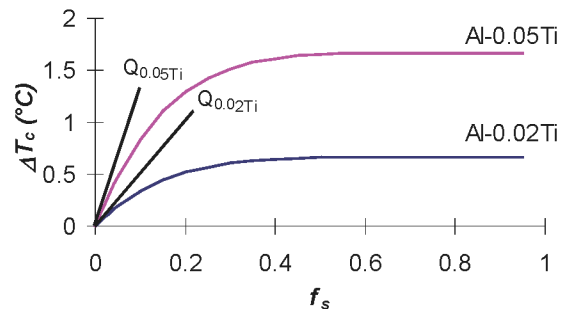


Figure 1. The development of the constitutional zone, ΔT_c , with fraction solid for Al-0.02Ti and Al-0.05Ti, assuming that Equation 1 describes accurately the magnitude of the constitutional zone and that Scheilian solidification behaviour occurs.

Equation 2 can be explained by considering the curve for the AlTi0.05 alloy in Figure 1. When a grain begins to grow the constitutionally undercooled zone increases as the undercooling below the liquidus, ΔT_c , increases along the AlTi0.05 curve. When it reaches a value of ΔT_c equivalent to ΔT_n at which the next nucleation event occurs, the value of f_s is f_{sn} and termed the RGS for that alloy at that ΔT_n .

Since RGS is a measure of f_s , by considering Figure 1, it can be seen that when powerful nucleants are present (ΔT_n is small), RGS is equivalent to $\Delta T_n/Q$. Therefore the grain size is inversely proportional to Q . This is possibly true when TiB_2 particles are present. However when poorer nucleants are present the accuracy of using Q to predict the effect of solute content on grain size will decrease. To improve the accuracy of prediction the actual value of f_{sn} at ΔT_n must be calculated using equation 2, rather than Q [9].

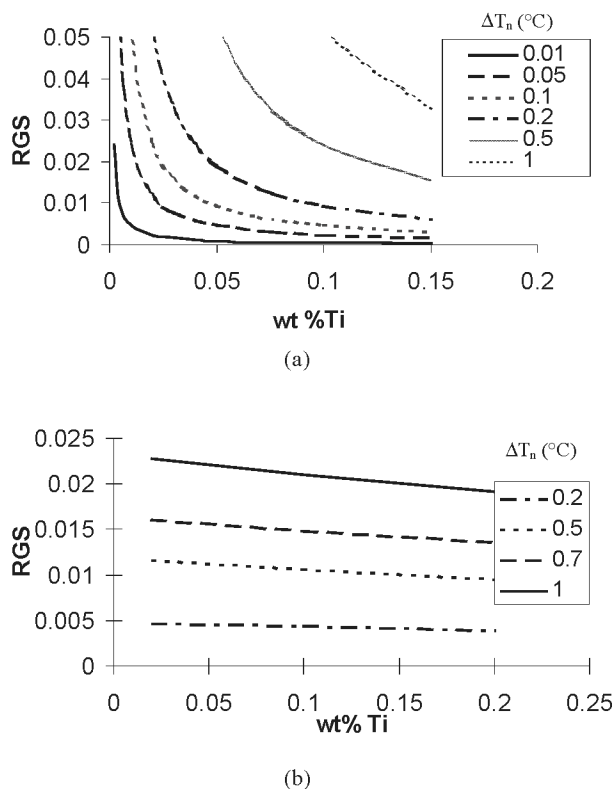


Figure 2. Predictions of the effect of titanium additions to the RGS of (a) pure aluminium and (b) AlSi7Mg0.3 alloy.

Equation 2 was used to produce Figure 2 (a) which shows how grain size is expected to decrease on the addition of titanium to pure aluminium for a variety of nucleant particle types having a range of ΔT_n values. However, the solidification of foundry alloys, such as AlSi7Mg0.3, is more complex and therefore the solidification behaviour cannot be modelled using equations for binary systems. Therefore the development of the constitutionally undercooled zone was calculated with the aid of temperature-fraction solid data derived from the Thermo-Calc® solidification

program. In the calculations, it was assumed that solidification occurred according to the predictions of the Scheil equation [15].

Figure 2 shows how differently changes in titanium content affect the grain size in pure aluminium compared with AlSi7Mg0.3. In pure aluminium the initial addition of titanium causes a dramatic decrease in the grain size with further additions producing diminishing reductions in the grain size. However in AlSi7Mg0.3, there is little decrease in the grain size with the addition of titanium. In both systems, the addition of more potent nucleant particles leads to a dramatic decrease in the grain size. These predictions show the same trends for Ti and TiB_2 additions as observed for actual measured grain sizes shown in Figure 3. This suggests that the difference in the grain refining behaviour of low solute wrought alloys and Al-Si foundry alloys is due to the relatively smaller effect the addition of titanium has on constitutional undercooling in Al-Si foundry alloys.

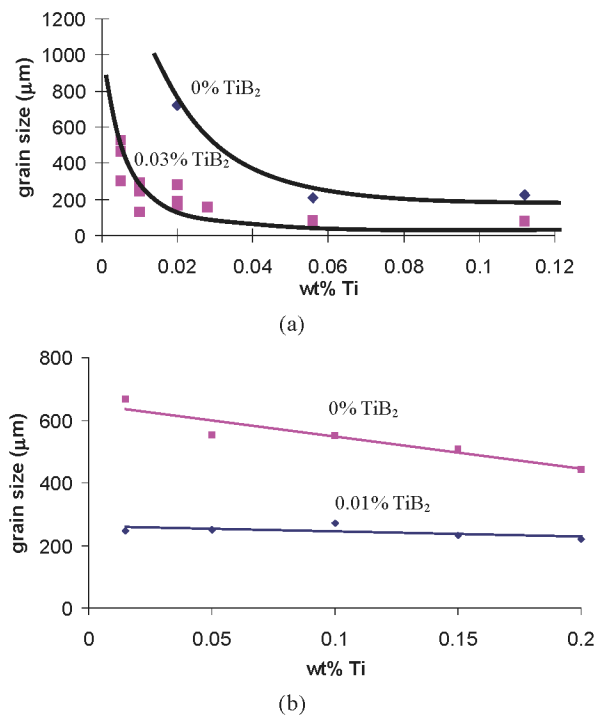


Figure 3. Measured grain size data for the addition of titanium to (a) 99.93% pure aluminium [5] and (b) AlSi7Mg0.3 alloy [16] both with and without the addition of TiB_2 nucleant particles.

Experimental

Whilst the model appears to describe the effect of solute on the grain size for pure aluminium and for an Al-Si foundry alloy, it has not been ascertained whether it is valid as a predictor of grain size for the addition of grain refiners to a wide variety of alloys. In this study five wrought alloys, which have a variety of alloying elements and Q values, were chosen to determine how closely a combination of elemental additions fit the model.

Table II. (a) The composition of the alloys produced, (b) the titanium and boron levels of each of the alloys after the various additions, and (c) the excess Ti contents of each of the alloys assuming all the boron in the alloy combines with titanium to form TiB₂. The compositions were measured using ICP-AES analysis.

(a)										
Alloy	Si	Cu	Fe	Mg	Cr	Mn	Al			
1050	0.2		0.27				balance			
2014	1.09	4.78	0.51	0.45		0.45	balance			
3003	0.55	0.12	0.58	0.01		1.37	balance			
5083	0.35		0.29	4.24	0.17	0.86	balance			
6061	0.83	0.21	0.05	0.73		0.01	balance			

(b)										
Alloy	No addition		TiB ₂		Ti1		Ti2		Ti3	
	%Ti	%B	%Ti	%B	%Ti	%B	%Ti	%B	%Ti	%B
1050	<0.001	0.003	0.003	0.004	0.006	0.003	0.018	0.003	0.058	0.004
2014	0.005	0.001	0.009	0.003	0.015	0.003	0.026	0.002	0.059	0.003
3003	<0.001	0.003	0.003	0.004	0.008	0.003	0.010	0.002	0.059	0.004
5083	<0.001	0.002	0.003	0.003	0.009	0.002	0.023	0.002	0.058	0.002
6061	<0.001	0.002	0.003	0.003	0.008	0.003	0.020	0.003	0.060	0.003

(c)										
Alloy	No addition		TiB ₂		Ti1		Ti2		Ti3	
	- %Ti excess	- %Ti excess	- %Ti excess	- %Ti excess	- %Ti excess	- %Ti excess	- %Ti excess	- %Ti excess	- %Ti excess	- %Ti excess
1050	0	0	0	0	0	0.012	0.05			
2014	0.003	0.003	0.003	0.009	0.009	0.02	0.053			
3003	0	0	0	0.002	0.002	0.004	0.053			
5083	0	0	0	0.005	0.005	0.019	0.054			
6061	0	0	0	0.002	0.002	0.003	0.037			

The alloys were produced from either 99.7% Al ingot or 6063 billet and by alloying with 75-80wt% element tablets for titanium, iron and manganese, and with commercial purity Mg ingot, Si lump and Cu rod. The five alloys made were 1050, 2014, 3003, 5083, 6061 and the compositions of each alloy are listed in Table II(a). All compositions are given in wt%.

The alloys were remelted in 1-2kg batches in a resistance furnace and cast into cylindrical graphite crucibles, 50mm in diameter and 50mm high and a wall thickness of 10mm [17]. The melt in the graphite crucibles was cooled between two pieces of fibrefrax so that a cooling rate of about 1°C/s was obtained [17]. Five ingots were cast from each melt: one without any additions, one after the addition of 0.007wt%Ti as AlTi3B1 master alloy (to obtain a TiB₂ addition of 0.005wt%) and then three after the addition of increasing levels of solute titanium (denoted Ti1, Ti2 and Ti3). An AlTi2 master alloy was made from 99.7% aluminium ingot and 75%Ti tablet and used for adding solute titanium, as most commercial titanium containing alloys, eg. Al6Ti, contain boron and carbon to increase the effectiveness of the master alloy, and for this work it was preferable to minimise the addition of impurity nucleant particles. After the addition of the master alloy, the melt was held for 10 minutes to dissolve any Al₃Ti particles present.

Metallographic samples were sectioned approximately 10mm from the base of the cast ingots, mechanically polished and anodised using a 0.5% HBF₄ solution for approximately 2 minutes at 20V. These samples were viewed optically with polarised light and the grain sizes were measured using a linear intercept technique. At least two fields were calculated for each measurement with up to 100 intercepts in each field. However,

when the grain size was large (>1000µm) fewer intercepts were counted.

Results

A constant addition of AlTi3B1 master alloy was made to each alloy so that the nucleant population was similar in each alloy. Therefore, the effect of solute additions could be studied independent of nucleant particle effects. However, as shown in Table II(b), the actual boron contents, as measured using 'Inductively Coupled Plasma – Atomic Emission Spectroscopy', (ICP-AES) were not exactly the same. The error due to the measurement method at these low levels of boron is probably a contributing factor to this variation. The addition of TiB₂ particles by the AlTi3B1 master alloy did not decrease the grain size in any of the alloys except in 2014 where equiaxed grains were obtained instead of columnar grains as observed in the other four alloys.

In Figure 4, the grain size of the alloys at each of the solute Ti addition levels (for a constant AlTi3B1 addition) is plotted against the titanium level from Table II(c). In all alloys, except 2014, the first addition of the AlTi2 master alloy (Ti1) caused the columnar to equiaxed transition (CET) to occur. Grain sizes above 1000µm were columnar and those below 500µm were equiaxed. Table II(c) shows that the first AlTi2 master alloy addition generated a level of titanium that is in excess of that required to form TiB₂. The base alloys contained titanium levels less than 2.2 times the boron levels (the weight ratio of Ti:B in TiB₂ is 2.2:1), except in

the 2014 alloy¹. Alloy 1050, at the Ti1 addition, according to the calculation in Table II(c), does not seem to have any excess titanium present despite its lower grain size. However, there may be some excess titanium present in 1050, because the resolution of the ICP analysis of the compositions is limited. Therefore it appears that the titanium content needs to be at least equivalent to the stoichiometric level of 2.2 times the boron content for the TiB₂ particles to nucleate aluminium.

The Q values for each of the alloys were calculated using both $\sum_i m_i c_{o,i} (k_i - 1)$ with the m and k values in Table I and using the initial rate of growth of the α -Al phase calculated from Thermo-Calc® data. These results are presented in Table III. There is a very close correlation between the two methods of calculating Q for these alloys, except in the case of 5083 where the addition of titanium increases at a greater rate than would be expected. However in 5083, other phases are precipitating out before and during the formation of the α -Al phase. The values of Q obtained from Thermo-Calc® were used for the analysis in the rest of this paper.

By comparing grain sizes in Figure 4 and the Q values in Table III it is seen that the grain size decreases with an increased Q value of the alloy, as expected. The alloy with the largest grain size for each of the additions was 1050, then decreasing through 3003, 6061, 5083 and finally 2014 with the smallest grain size.

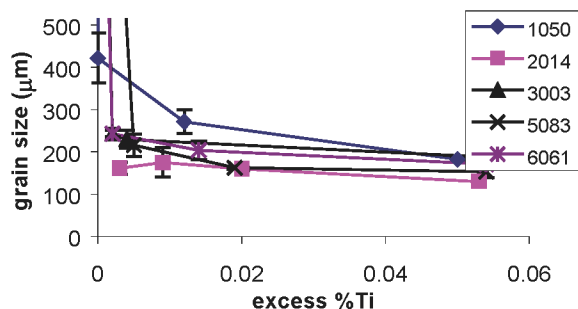


Figure 4. The measured grain size results for each of the alloys plotted against the titanium level in excess of that required to form TiB₂.

In Figure 5, the grain size results are plotted against the Q values presented in Table III. Apart from the first point, corresponding to the AlTi3B1 addition, where in all alloys, except for 1050, there is no excess titanium, the grain size decreases with the Q value of the alloy. At higher Q values the rate of decrease in the grain size on further increases in Q decreases, to a point where there is almost no further decrease in the grain size.

Since the values of ΔT_n are not known for the nucleants, it is assumed that Q is indicative of the effect of solute on the grain size. Earlier it was suggested that this is the case when extremely potent nucleants are present, and TiB₂ particles are known to be very potent nucleant particles in aluminium. If this is the case then the model predicts that the grain size is inversely proportional to Q. A curve of this form has been plotted on Figure 5 so that it fits the data as well as possible.

¹ Boron scavenges titanium atoms to form the very stable compound TiB₂.

The general form of the predicted grain size curve appears to be similar to the experimental data, in that there is an initial rapid decrease in the grain size and then as Q increases the grain size continues to decrease but more slowly. However, it appears from the curve plotted on Figure 5, that the model predicts a slower rate of decrease in the grain size at lower Q values and then predicts that for higher Q values the grain size continues to decrease more rapidly than for the experimental results. The experimental results appear to show a grain size decreasing very slowly at increasingly higher Q values to some positive value, whilst the model predicts that as Q increases towards infinity, the grain size will decrease towards zero.

Table III. Growth restriction factors of the alloys as calculated using the sum of the individual growth restriction factors, $\sum_i m_i c_{o,i} (k_i - 1)$, and using Thermo-Calc® to calculate the initial rate of increase in the constitutional undercooling.

Alloy	$\sum_i m_i c_{o,i} (k_i - 1)$	$\frac{d(\Delta T_c)}{df_s}$ (Thermo-Calc®)
1050	1.96 K	1.86 K
+0.001Ti	2.18	2.18
+0.012Ti	4.60	5.65
+0.05Ti	12.96	17.43
2014	22.69	21.89
+0.003Ti	23.35	24.04
+0.009Ti	24.67	25.62
+0.02Ti	27.09	27.89
+0.05Ti	33.69	36.47
3003	5.41	6.60
+0.002Ti	5.85	6.91
+0.004Ti	6.29	7.10
+0.05Ti	16.41	18.10
5083	16.35	20.60
+0.005Ti	17.45	24.06
+0.019Ti	20.53	34.06
+0.05Ti	27.35	67.16
6061	7.83	7.55
+0.002Ti	8.27	8.07
+0.014Ti	10.91	10.57
+0.04Ti	16.63	18.48

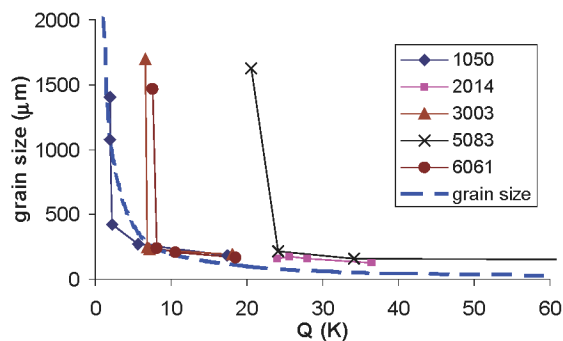


Figure 5. The measured grain size of the alloys plotted against Q as calculated by Thermo-Calc®, for each value. A grain size vs. Q curve as predicted by the model is also plotted.

Figure 6 plots the grain sizes obtained experimentally against $1/Q$, except for those with Ti contents below stoichiometric TiB_2 concentrations. It is found that the relationship between grain size and $1/Q$ is very linear, although it does not pass through the origin. In other words, the grain size is a function of $1/Q$, but there appears to be a lower limit for the grain size achievable. This minimum grain size is obtained by the intercept on the vertical axis, i.e. where Q is infinite. In the case of the experimental data presented here, the lower limit in grain size appears to be $145\mu m$. Chai et al [13] found a similar result for Al-Cu alloys, although the lower limit in grain size was close to $70\mu m$.

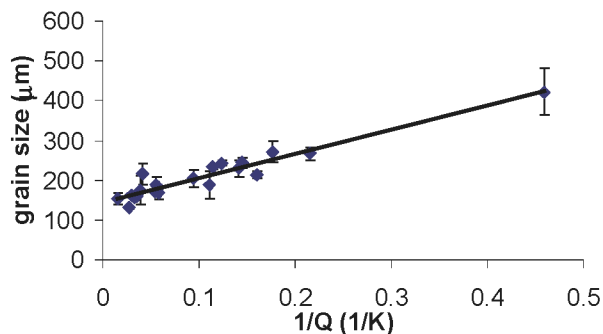


Figure 6. A compilation of the grain size data for all the alloys when some excess titanium was present plotted against the reciprocal of Q . A trendline has been placed through the data.

Discussion

It has been found that when TiB_2 particles are present the grain size of an alloy is closely related to its solute content as measured by Q . This relationship appears to be independent of which solute elements are present or the combination of elements present in the alloys tested. However, there are two particularly interesting findings: the titanium content must be at least at the Ti:B ratio of 2.2:1 for the TiB_2 particles to nucleate α -Al and that there appears to be a lower limit in the grain size achievable.

The fact that at least stoichiometric levels of solute titanium appear to be required for nucleation on the TiB_2 particles could be considered as evidence for the hypothesis that TiB_2 particles require a layer of Al_3Ti on the surface to be effective nucleants [18, 19]. Whilst this appears to be a plausible explanation, the very low levels of titanium required for this to occur is interesting. The result poses the question as to whether 10ppm titanium or less is sufficient to produce an Al_3Ti layer on TiB_2 particles and dramatically change the nucleation characteristics? However, it has also been found in Al-Si casting alloys that AlB_2 particles are effective nucleants without the presence of titanium [20-22] from which it can be extrapolated that TiB_2 particles (which are isomorphous to AlB_2 [22]) should also be able to nucleate α -Al, even in wrought alloys.

The boron levels present in the experimental alloys are below the eutectic point in the Al-B phase diagram of 0.022%B [22]. Therefore AlB_2 should not be present as a nucleant particle. On addition of titanium it would be expected that boron would

combine with the titanium because TiB_2 is the most thermodynamically stable of the borides likely to be present in an aluminium alloy [23]. Once TiB_2 particles are formed then nucleation should be able to occur on the surface of these particles. $(Al,Ti)B_2$ particles have been found to form when there is not enough titanium to form TiB_2 and these particles are known to be good nucleants in Al-Si foundry alloys and are stable to lower boron compositions than AlB_2 particles [22]. Therefore it is likely that in the alloys studied that boron remains in solution unless it combines with titanium to form TiB_2 or the mixed boride $(Al,Ti)B_2$, because the boron content is too low to form AlB_2 .

Instead of titanium contents being required in excess of the amount to form TiB_2 for nucleation, the results may also be interpreted that boron in solution poisons nucleation. It is known that V, Cr and Mn form borides which are less thermodynamically stable than TiB_2 particles but more stable than AlB_2 [23]. Therefore the initial boron content will combine with titanium to form TiB_2 particles. After the titanium atoms are exhausted, if there is still boron present, then the boron will combine with vanadium to form VB_2 and then manganese to form MnB_2 and chromium to form CrB_2 . These borides may coat the TiB_2 particles making them inactive. Alloys 2014, 3003 and 5083 all contain significant amounts of manganese and 5083 contains some Cr. Alloy 6061 contains only 0.01%Mn, which seems hardly significant, but since there is only 0.003%B present, it may be enough manganese to form a poisoning MnB_2 layer on the TiB_2 nucleants. V is a common impurity in all aluminium alloys. It appears that once there is sufficient Ti to consume all the boron as TiB_2 then the CrB_2 and MnB_2 layers do not form and the TiB_2 particles become active. This is confirmed by Figure 6 which shows that grain size has no dependence on the elemental make-up of the alloys.

The finding of a minimum grain size that can be achieved on the addition of further solute as shown in Figure 6, is an important result. Whilst it may be assumed that there is a lower limit to the grain size achieved in all castings, it would be interesting to ascertain the reason for this limit and the factors affecting it. The grain refinement data published previously has found that there are definitely diminishing returns on the addition of further grain refiner, if not a minimum limit to the grain size [5, 6, 13, 24], however, the authors did not explain the reason for it. The models of Maxwell and Hellawell [3] and Greer et al [4] also have the grain size diminishing if not having a lower limit. In these models the grain size is limited by latent heat evolution, i.e. recalescence. The fact that the grain size continues to follow the $1/Q$ relationship to high values of Q implies that there is no shortage of potent nucleant particles. If there was a shortage the grain size would deviate from the $1/Q$ relationship towards a larger grain size.

The lower limit in grain size found in the present results suggests that even if there is an instantaneous increase in the amount of undercooling as a grain begins to grow, there is a limit to how close the next grain will nucleate. The reason may be due to the magnitude of the thermal and compositional diffusion fields and in turn the solidification conditions. Further analysis of grain size data for different cooling conditions is required before the reason for, and the factors affecting, the minimum grain size can be determined.

Conclusions

A model previously developed which relates the solute level in an alloy and the nucleant potency (inversely proportional to ΔT_n) to the relative grain size suggested that, for very potent nucleants, $1/Q$ is a good estimate of the effect of the alloy solute content on the grain size. This prediction was validated by experimental data for five different wrought alloys (1050, 2014, 3003, 5083 and 6061) with a constant TiB_2 addition and several excess titanium solute levels. The measured grain sizes were plotted against $1/Q$ and a linear relationship was found as predicted by the model.

It was also found that there is a minimum grain size, for this casting configuration, below which extra addition of solute is unable to decrease the grain size further. The reasons for the minimum grain size are currently unclear but may be due to recalescence or the size of the thermal and solute diffusion fields.

It appears that the TiB_2 particles were not active nucleants until there was sufficient titanium to consume all the boron as TiB_2 . It is speculated that at sub-stoichiometric levels of titanium the excess boron forms the less stable borides of manganese and chromium on the surface of the TiB_2 particles thus poisoning them.

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