Role of Undercooling and Effect of Solute Particles on Grain Refinement of Aluminium Alloys

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Introduction
Grain refinement is an imperative technique used in industries to reduce the size of grains of the as-cast alloys. The main aim of grain refinement is to suppress the growth of columnar and twin columnar grains and encourage a structure having equiaxed grains[1-3]. This is because a structure having fine equiaxed grains will have desirable mechanical properties and better feeding characteristics[3]. Grain refinement has many benefits in direct chill casting operations too; this includes reduced hot tearing susceptibility and reduced homogenisation time[3].

Finer grains are achieved by the addition of grain refiners which are generally added in the form of master alloys such as Al-5Ti-1B for aluminium alloys. The effect of grain refiners can be divided into two: nucleant effect and solute effect[4]. These grain refiners contain inoculants particle (TiB₂, TiC)[4-6] which as heterogeneities in the melt provide nucleation surfaces. This can be characterised as the first step of grain refinement i.e. nucleant effect[7]. The solute effect comes into play once nuclei starts to grow. In pure aluminium, there are no segregating elements present; hence, there is no constitutionally undercooled zone in front of the interface to promote nucleation of aluminium on the nucleant particles (TiB₂). But when solute is present, TiB₂ becomes an effective nucleant due to the constitutionally undercooled zone. Therefore, when Al-5Ti-1B is added to an alloy, TiB₂ particles which act as nucleant particles will be coated with a thin layer of Al₃Ti. Generally, commercial alloys containing 5 to 10% Ti are primarily a mixture of α-aluminium and crystalline TiAl₃, α-aluminium forms at the surface of the TiAl₃ particle at temperature below the melting point of the bulk metal. Once solid has formed, the TiAl₃ particle is engulfed in the solid phase, and further growth becomes limited. Therefore, TiAl₃ helps in improving the ratio of nucleation rate to growth rate as now large number of nucleating sites are present, hence there’ll be greater number of nuclei forming at the same time and as they grow, the constitutional undercooling zone, which develops ahead of solid-liquid interface, permits the nucleation on heterogeneities lying within the zone. On further growth of these nuclei, the particles will begin to impinge each other thus restricting the growth and increasing the ratio. Hence, fine grains are produced.

Grain refinement is an important technique to produce fine equiaxed grain structure in order to obtain desirable mechanical and foundry properties. This is achieved by addition of grain refiner (Al-5Ti-1B) in the form of master alloy. Constitutional undercooling results when solid freezes with a composition difference from that of liquid from which it forms. The mechanism of grain refinement is addressed by nucleant and solute paradigm. In nucleant paradigm, nucleating particles are responsible for achievement of finer grains. However, grain refinement is very sensitive to the alloying elements present. This is explained by solute paradigm. The growth restriction effects of the solute are quantified by two parameters, i.e. growth restriction factor, Q and the undercooling parameter, P. The growth restriction factor Q is proportional to the initial rate of development of constitutional undercooling zone and can be used directly as a criterion for the grain refinement in the aluminium alloys. P gives the maximum undercooling which can be generated by a particular concentration of grain refiner. Q is inversely related to the resultant grain size. The nucleation paradigm is also recognised as a part of process. To fully explain the mechanism of grain refinement, it is essential to study solute effect on grain refinement. In the present study, nucleant effect and solute effect have been studied on Al alloys to understand how Q, P, relative grain size and grain size are related.

Keywords: Constitutional undercooling, Growth restriction factor, Undercooling parameter, Solute effect, Nucleation.

Solute theory says solute elements like titanium segregate to the inoculant/melt interface and affect the growth of dendrites and also affect the constitutional undercooling at the solid-liquid interface. It is expressed by GRF which is a measure of the growth restricting effect of solute elements on the growth of solid-liquid interface. The growth restriction effects of solute can be quantified by growth restriction parameter (GRF) represented by Q and
undercooling parameter represented by $P^{[8-10]}$. $P$ is the maximum degree of undercooling that can be generated and be given by:

$$P = \frac{m_l C_0 (k-1)}{k}$$

where $m_l$ is the slope of liquidus curve in binary phase diagram, $C_0$ is the bulk concentration and $k$ is a constant known as partitioning coefficient.

The growth-restriction parameter $Q$ is in inverse proportion to the growth rate. The concentration of Ti with other elements leads to a constitutionally undercooled zone in front of the growth interface and interrupt the growth of the previous grains. Being inversely proportional to growth rate, it is also affected by the segregating ability of solute and concentration of bulk and is given by:

$$Q = \frac{m_l C_0 (k-1)}{k}$$

$Q$ can be taken as a parameter to measure the grain size. Higher the $Q$ for a solute, lesser is the grain size for that alloy$^{[11-13]}$. The present paper briefly studies the relationship between $Q$, $P$, relative grain size and grain size for aluminium alloys. The work by Easton and St. John$^{[14, 2]}$ proposed that the grain refinement is simply related to the potency of a nucleant, the degree and rate of development of constitutional undercooling generated due to solute rejection during growth of previously nucleated grains.

**Constitutional Undercooling**

Solidification of metal during casting in industries is the most practical example of freezing liquid metal which is poured into a mould cavity and freezes as a consequence of heat losses through the mould shell. As a result, the temperature is always the lowest at the mould walls and rises towards the centre of the mould. Solidification accordingly, starts at the walls and proceeds inward.

In solid solution alloys, solidification occurs over a range of temperature, unlike pure metals which solidify at a single freezing point. This range is called freezing range and is bounded by a liquidus line (at which solidification starts) and a solidus line (at which solidification ends) as shown in Fig.1c. This freezing range is characterised by the equilibrium partitioning ratio $k$, where $k = C_s/C_l$. It defines how the solute alloy partitions between solid and liquid phases. The freezing range depends on composition within the system and also on the two component metals.

During the solidification of a solid solution alloy under foundry condition, there will be a liquid build-up solute atoms in the liquid next to the advancing solid interface. In this case, undercooling which flourishies the driving force for dendritic growth, is normally of different type. Thermal undercooling can also be a factor in freezing of an alloy, but constitutional undercooling, which should now be considered, is of much greater importance. Constitutional undercooling results when solid freezes with a composition difference from that of liquid from which it forms.

The situation is illustrated in Fig.1b where the temperature of melt is assumed to rise linearly with distance from the interface. A second curve in Fig.1b shows the freezing point of the melt as a function of distance from the interface. This varies with the distance from the interface, due to the change in composition of the liquid as one moves away from the interface. At the interface, the freezing temperature is $T_s$ but away from the interface, it at first rises rapidly and then levels off to the temperature $T_L$, the temperature at which the bulk of liquid will begin to freeze. As shown in Fig.1b, the temperature of liquid and freezing point of the liquid intersect at two points : (i) at the interface and (ii) at the distance $x$ from the interface.

The pertinent point, however, is that within the distance $x$ the liquid lies at a temperature below its freezing point. Inside this range, it is effectively super-cooled in spite of the fact that the temperature gradient is positive. This is direct result of concentration gradient in the liquid alloy in front of interface. Since, this undercooling arises from the change in composition, and not temperature, which is why it is called constitutional undercooling.

Let us now quantitatively develop the criteria for constitutional undercooling. Considering Fig.1c which shows the relation between the constitutional phase diagram for a binary alloy and constitutional undercooling on solidification, the original melt of composition $C_0$ starts to freeze at $T_i$. The first solid to appear has a composition $kC_0$, where $k = C_s/C_l$.

On forming solid that contains $kC_0$ amount of solute, the solute remaining in the liquid has to be rejected ahead of advancing front. Thus, although the liquid was initially of uniform composition $C_0$, after an advance of about a millimetre or so, the composition of the liquid ahead of
front builds up to peak value of \( C_0/k \) (since \( k = C_s/C_0 \)). This is the steady-state condition. Grain refinement is influenced by two parameters namely growth restriction factor and undercooling parameter which are discussed below.

**The Two Parameters**

1. **Growth Restriction Factor, Q**

   It is the build-up of solute at the solid liquid interface that restricts the growth of grains and therefore, it becomes necessary to quantify its effect using GRF. The growth-restriction parameter \( Q \) is inversely proportional to the growth rate\(^{[11]} \). The constitutional undercooling (\( \Delta T_c \)) produced due to solute segregation can be related to the solid fraction \( (f_s) \) i.e fraction of solid formed in the melt or the amount of solid formed in the melt by solidification of molten metal, by Scheilian solidification relation which is given as\(^{[15,8]} \)

   \[
   \Delta T_c = m_l C_0 \left[ 1 - \frac{1}{(1-f_s)k} \right]
   \]

   Where \( m_l \) is the slope of liquidus curve in binary phase diagram, \( C_0 \) is the bulk concentration and \( k \) is a constant known as partitioning coefficient.

   In the beginning of solidification, fraction of solid formed is very little such that \( f_s = 0 \). Therefore, differentiating above equation with respect to (w.r.t) fraction of solid formed gives us the relation:

   \[
   \frac{d\Delta T_c}{df_s} = m_l C_0 (k-1)
   \]

   which is growth restriction factor, \( Q \).

   The rate at which the undercooled zone develops at the beginning of solidification is equal to the growth restriction factor. From the above relation, it can be said that as \( Q \) increases, the maximum undercooling which can be generated increases, also there's an increase in the development rate of the constitutional undercooling zone and with it the time required for the nucleation to begin on the present nucleants within the undercooled region decreases, this will result in a structure with desired finer grains.

2. **Undercooling Parameter, P**

   \( P \) is the maximum amount of undercooling which can be generated by a growing grain due to segregation of solute. If the grain refiner added is strongly effective, then the maximum undercooling which can be achieved by it is more. It is used to compare the effects of different solute elements at different concentrations and can be denoted as\(^{[8]} \):

   \[
   P = m_l C_0 (k-1)/k = Q/k
   \]

   where symbols used have their usual meaning.

**Why \( Q \) is Preferred over \( P \)?**

Both of the above two factors, \( P \) and \( Q \), can be used as a measure of grain size. But in practical cases, GRF is preferred over \( P \). This is because the deviation obtained in the values of \( P \) for varying solute content comes out to be much greater than the deviation shown by \( Q \) values for the same. It can be understood from the following Fig. 2a and 2b.\(^{[10, 16]} \)

Figures 2a and 2b show the plot of \( P \) and \( Q \) values with the grain size respectively. It can be seen that for the binary alloys inoculated with a grain refiner, decrease in grain size with increasing \( P \) and \( Q \) values follows same trend but the degree of scatter in \( P \) values is much greater than in \( Q \) values. For example: at grain size of 200 \( \mu \)m, the data range for \( Q = 1.5-4K \) and for \( P = 0.25 \) to 30K\(^{[16]} \). Therefore, both factors give the accurate estimate of grain size but GRF is more precise than \( P \).
Relation between GRF, Grain Size and Nucleant Potency

Nucleant potency can be described as the ability of a substrate to facilitate the nucleation on its surface\[11\]. The degree of undercooling required by a substrate decides whether it is a strong or weak nucleant. Following Fig. 3 is the phase diagram for the dilute binary system where k and m₁ are assumed to be independent of solute content.

Fig. 3: [4, 11, 17] Phase Diagram.

Here, it is also assumed that the thermal gradient in front of solid-liquid interface is zero and thus there’s no thermal undercooling and latent heat\[11, 18\]. Therefore, the maximum undercooling at a solute concentration \(C_s^\ast\) can be given by:

\[
\Delta T_C = T_m - T_{actual} = T_m - m_1 C_0 - (T_m - m_s C_s^\ast) \quad \text{(1)}
\]

Where, \(\Delta T_C\) is the maximum undercooling at a solute concentration \(C_s^\ast\), \(T_m\) is the liquidus temperature at which solidification begins, \(T_{actual}\) is the actual temperature of the melt, \(m_1\) and \(m_s\) are the slopes of liquidus and solidus respectively, \(C_0\) and \(C_s^\ast\) are the concentration of solute in bulk and the solid formed and k is the solute partitioning coefficient which is given by:

\[
k = \frac{C_s^\ast}{C_s^0} \quad \text{(2)}
\]

From the solid redistribution equation\[14\],

\[
C_s^0 = C_0 \left[ 1 - (1 - k) \exp \left( -\frac{k \nu}{D_1} x \right) \right] \quad \text{(3)}
\]

Where \(D_s\) is the diffusion coefficient of solute in liquid phase, x is the solid growth distance and \(\nu\) is the growth rate of solid using the Equation 2 and 3 a relation is established which is given as:

\[
\Delta T_C = m_1 (C_0 - \frac{C_s^\ast}{k}) \cdot \frac{m_s C_0 (k-1)}{k} (1 - \exp \left( -\frac{k \nu}{D_1} x \right)) \quad \text{(4)}
\]

From this relation, it can be seen that when the solid growth distance (x) increases, the undercooling generated ahead of front (\(\Delta T_C\)) increases.

The variation of constitutional undercooling with the solid growth distance can be depicted from the above Fig. 4 for AlTi0.05, AlTi0.10 and AlTi0.15 alloys which can be used as effective grain refiners in industry. It can be seen that the initial increase rate in \(\Delta T_C\) is much faster for AlTi0.15 alloy than that of the AlTi0.10 alloy, while it is faster for AlTi0.10 alloy than that of AlTi0.05 alloy. Thus, as the amount of solute (Ti) increases \(Q\) (slope of the curve) increases and so is the rate with which maximum undercooling, P is achieved.

Fig. 4: Development of the constitutional undercooling zone \(\Delta T_C\) with solid growth distance x for AlTi0.05, AlTi0.10 and AlTi0.15 alloys\[2\]

Fig. 5: Development of the constitutional undercooling zone \(\Delta T_C\) with solid growth distance x for AlTi0.10 and AlTi0.15 alloys\[2\]

For a certain nucleant particle, let the required amount of undercooling be \(\Delta T_n\), as shown by the red coloured line, this amount of undercooling is achieved at a solid growth distance OX by the grain refiner containing 0.15%Ti and
at a distance equal to OY by the grain refiner containing 0.10% Ti. Since OX is less than OY therefore, we can say that finer grains are achieved by stronger nucleant, having greater concentration of solute, thus having higher Q value.

Let \( x_n \) be the solid growth distance at which the undercooling generated reaches to \( \Delta T_n \), the amount of undercooling needed for the nucleation to begin on the adjacent nucleant substrates. \( x_n \) is taken as the measure of the grain size upto which grain will grow before subsequent nucleation on the adjacent nucleants will begin as the distance between adjacent effective nucleation determines the grain size in the final microstructure. To compare the effect of solute content and the potential of the nucleants, \( x_n \) is taken as the relative grain size (RGS) which is different from average grain size as RGS gives us an estimate of the average grain size for a microstructure containing weak nucleants. When the undercooling generated reaches to \( \Delta T_n \), RGS can be given by:

\[
x_n = \frac{D_1}{k_1} \ln \frac{P^\Delta T_n}{P}
\]

(5)

Here, the effects of latent heat and thermal gradient have been neglected which tends to reduce the effective undercooling and the size of undercooled zone. If the nucleant shows a strong potential for nucleation, then \( \Delta T_n \) required by it will be low and much less than the maximum undercooling which can be achieved i.e P and so can be achieved easily at a smaller grain size (Fig.4). The Q can be taken as a direct measure of RGS for the case where strong potential nucleants are used, this is because for them it can be assumed that \( \Delta T_n \ll P \). When this assumption is applied to Eq.5 it comes out that

\[
RGS = x_n = \frac{D_1 \Delta T_n}{QV}
\]

(6)

That is,

\[
RGS \propto \frac{1}{Q}
\]

(7)

Hence, RGS has a direct relation with Q (only for the strong nucleants) and therefore, the above stated fact is proved. The Eq.7 also shows that as the GRF increases, the RGS decreases for a strong nucleant. But the same cannot be said for weakly potent nucleants as for them \( \Delta T_n \approx P \), so, unlike strong nucleants Q cannot be related directly with RGS for weak nucleants and therefore, only RGS which will be the function of P, can be used as an appropriate measure of grain size and not Q. It can also be concluded that strong nucleants require lower degree of undercooling for their activation as heterogeneous nucleation sites and their addition results in finer grain structure when compared to weak nucleants. Figure 6a shows predicted value of relative grain size with Ti content in Al-Si alloys and Fig.6b gives the actual grain size for the same alloy at two different concentration of TiB_2[16].

Fig.6a: Predicted value of relative grain size with Ti content in Al-Si alloys.

Fig.6b: The actual grain size and Ti concentration plot for the same alloy at two different concentration of TiB_2[16].

It can be seen that both RGS and actual grain size follows same trend with varying Ti content except the actual grain size becomes constant at higher values of Ti concentration. Therefore, RGS can be taken as an appropriate measure of actual grain size. The decrease in RGS for strong nucleants (low undercooling needed) increases with increase in Ti content and is greater as compared to weak nucleants. It is also seen that with increase in TiB_2 content there’s a drastic decrease in grain size and hence, it is concluded that presence of both Ti and TiB_2 is important for effective grain refinement.
Fig. 7a: Schematic diagram showing relative grain size and process of nucleation on nucleating particles in undercooled zone.

Here, two situations are compared at different instants of time. Figure 7a shows that initially as the grain grows and reaches to a point where the amount of undercooling achieved is the undercooling needed by the inoculant particles for the beginning of nucleation on their surface, at this instant the size of the grain is referred to as the relative grain size. Figure 7b is at a later point of time when the grain shown in Fig. 7a has grown and the undercooling achieved is equal to P, the maximum undercooling which can be achieved and the nucleated particles nearby impinge with each other thus restricting the growth.

Relationship between Grain Size and Q

The relationship between the grain size and growth restricting parameter can also be empirically given as:

\[ d = a + \frac{b}{Q} \] .............................. (8)

Where a and b are constants and d is the grain size. It should be noted that this relationship is different from the one between RGS and GRF which was previously stated in section 4. The relationship between grain size and GRF shows that the grain size varies linearly with the inverse of growth restricting parameter and therefore Eq.8 can be compared to the equation of line

\[ y = mx + c \] .............................. (9)

On comparing both the equations, it can be said that a-term is the intercept whereas b-term is the slope of line as depicted by Fig. 8 and hence along with Q both of these factors are also important in determining the grain size.

Easton and St. John\textsuperscript{19,14} suggested that after the initial nucleation of grains in the thermally undercooled region at a mould wall, a wave of nucleation events occurs from the edge of a casting to the thermal centre as the constitutional undercooling reaches the undercooling needed by the nucleant to activate i.e. \( \Delta T_n \). This requires, although small, but growth of already nucleated particles which is related to the fraction solid as\textsuperscript{19}:

\[ Q = \frac{\Delta T_n}{d_f} \]

Therefore, nucleation of grains in a constitutionally undercooled zone indicates that the b-term is related to the amount of undercooling needed for the nucleation to begin on the adjacent nucleant substrates or the potency of the substrates in the melt\textsuperscript{19}. Whereas a-term, unlike b-term, depends upon the nucleant particle concentration, because a-term is that grain size at which the grain refinement effect of solute is maximum i.e. the heterogeneities begin nucleation on their surface as soon as they fall within undercooled zone. Hence, the intercept is dependent on the only other variable which will affect actual grain size i.e. distances between the active nucleation sites. a-term represents the maximum number of particles.
within a set addition of a particular type of refiner that are able to facilitate nucleation which in turn affects the grain size. More the number of active nucleation sites, smaller will be the grain size. By assuming that the grain density (number of grains per unit volume) is proportional to the nucleant particle density (number of nucleant particles per unit volume of the melt), it would be expected that the linear intercept grain size, \( \alpha \), is proportional to \( \frac{1}{\rho f_n} \), where \( \rho \) is the density of particles and \( f_n \) is the fraction of those particles that are active and can nucleate a grain. Hence, there is an inverse cube root relationship between the number of particles present and the grain diameter, which is proportional to the grain size. The complete relationship can be denoted by [19]:

\[
d = \frac{3}{\sqrt[3]{1/\rho f_n}} + \frac{b \Delta T_n}{Q} \tag{10}
\]

For Al alloys with Al-5Ti-B master alloy, following relationship can be used to determine the grain size [19]:

\[
d = \frac{43}{\sqrt[3]{1/\rho f_n}} + \frac{520}{Q} \tag{11}
\]

The value of b-term for this grain refiner is lower when compared to b-term value for Al-3Ti-B which is 650 but at the same time, the value of a-term is higher for the former grain refiner. This shows that Al-5Ti-B will be more effective for low solute concentrations as compared to Al-3Ti-B, as it has numerically greater coefficient for the first term. This kind of analysis may provide a tool for comparing and optimising the effectiveness of grain refiners.

**Summary**

There are four factors which must be considered by shop-floor engineers while choosing a grain refiner for refinement of grain size:

1. Growth Restriction Factor, Q: Higher the growth restriction factor of a grain refiner at certain melt composition, finer will be the grains produced.
2. Undercooling Parameter, P: It is the maximum undercooling which can be produced by a grain refiner at certain composition. Greater the undercooling parameter, stronger will be the grain refiner.
3. \( \Delta T_n \): The amount of undercooling needed for the nucleation to begin on the adjacent nucleant substrates decides whether a given nucleant is strong or weak. It is low for strong nucleants and high for weak nucleants.
4. Relative Grain Size, RGS: It gives an estimate of the grain size resulting from the addition of certain grain refiner to the melt. Lower RGS is generally preferred.

**References**