

 Open access • Journal Article • DOI:10.1016/J.COSSMS.2015.10.001

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Published on: 01 Feb 2016 - Current Opinion in Solid State & Materials Science (Elsevier)

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Recent Advances in Grain Refinement of Light Metals and Alloys

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Abstract

Grain refinement leads, in general, to a decreased tendency to hot tearing, a more dispersed and refined porosity distribution, and improved directional feeding characteristics during solidification. Reduced as-cast grain size can also lead to improved mechanical properties and wrought processing by reducing the recrystallized grain size and achieving a fully recrystallized microstructure. It is now well established that the two key factors controlling grain refinement are *the nucleant particles* including their *potency, size distribution and particle number density*, and the *rate of development of growth restriction, Q, generated by the alloy chemistry* which establishes the undercooling needed to trigger nucleation events and facilitates their survival. The theories underpinning our current understanding of nucleation and grain formation are presented. The application of the latest theories to the light alloys of Al, Mg and Ti is explored as well as their applicability to a range of casting and solidification environments. In addition, processing by the application of physical processes such as external fields and additive manufacturing is discussed. To conclude, the current challenges for the development of reliable grain refining technologies for difficult to refine alloy systems will be presented.

Key Words: nucleation; crystal growth; ultrasonic treatment; aluminium alloys; magnesium alloys; titanium alloys; pulsed magneto-oscillation; X-ray radiography; additive manufacturing.

1. Introduction

Grain size is one of the key microstructural factors that affects the processing and properties of alloys. A fine grain size leads, in general, to a decreased tendency to hot tearing [1-3], a more dispersed and refined porosity distribution [4, 5], and improved directional feeding characteristics [6], although it can also reduce fluidity [7] and cause defects in hot spots [8]. Reduced as-cast grain size can also lead to improved properties, e.g. strengthening through the Hall-Petch relationship, improved wrought processing by reducing the recrystallized grain size and achieving a fully recrystallized microstructure more easily. There are situations where it is preferable to minimize or even remove grain boundaries, e.g. to improve creep resistance, but this is the exception rather than the rule. In any case, it is important that the grain size can be engineered rather than being just a consequence of alloy and processing.

It has been recognized for almost 100 years that the alloy constitution and the processing conditions are important factors influencing the grain size obtained [9-12]. In early studies it was found that the addition of other elements to a metal prior to solidification generally leads to a transition from columnar to equiaxed grain morphologies (CET), although the effects of second phases and eutectics were also observed. Concepts such as growth restriction were already in use and the competition between grain growth and nucleation was already determined to be key to the attainment of a fine grain size [12]. The modern grain refiners for Al-based alloys were an outcome of the work of Cibula [13, 14], who focused on identifying potent nuclei. He used the work of Eborall [15] who identified Ti as a particularly effective grain refining alloying element at concentrations below the peritectic composition which indicated that there must be effective nucleants present. He proposed that this was due to the presence of boron and carbon and was able to identify the Al-Ti-B grain refining system, which is still used for grain refining Al-based alloys.

At approximately the same time, the importance of peritectic systems for grain refinement was identified [16], which led to a continuing discussion of the role of the peritectic reaction on grain refinement [17], including the continuing controversy over whether an Al_3Ti layer is required on TiB_2 particles to make them active [18-25]. Concurrently, theories related to understanding constitutional supercooling (CS) were

developed [26-29] and as shown recently [30] have become critical to understanding grain refinement.

From this point in time, grain refinement research focused on the key issues of identifying nucleant particles and the role of alloy constitution with a number of attempts at bringing these two factors together into grain refinement models [31-34]. At times research would often emphasize one effect over the other sometimes leading to a wide variety of theories being proposed [31], but it is now clear that if both factors are considered (along with the role of processing conditions) comprehensive grain refinement models can be developed to properly describe the grain formation process.

This paper initially introduces recent theoretical developments in grain refinement that incorporate both nucleant particles and solute, after which the details of the role of solute and of inoculants are discussed. Recently, there has been increased interest in the role of physical processes, such as stirring, ultrasonic treatment and electromagnetic forces on grain refinement, which are reviewed. The role of advanced experimental techniques in understanding grain refinement is discussed and finally some of the outstanding challenges including approaches to grain refinement in additive manufacturing are considered. It should be noted that grain refinement mechanisms in particular alloy groups have been well described in review papers [31, 35-40], which should be consulted if readers would like to understand grain refinement in particular alloy systems.

2. Current understanding: the role of solute on grain refinement

Over the last two decades our understanding of the mechanisms of grain refinement has been continually improving. It is now well established that the two key factors controlling grain refinement are *the nucleant particles* including their *potency, size distribution and particle number density*, and the *rate of development of growth restriction, Q , generated by the alloy chemistry* which establishes the undercooling needed to trigger nucleation events and facilitates their survival. Greer et al.'s Free Growth model [33] is now commonly used to determine the potency of particles (see Section 3). They also investigated the effect of Q for isothermal melts [41, 42] (discussed later in this Section). Recently, the Interdependence Theory was developed that incorporates both particle and constitutional factors into one relationship that represents the particles and solute by their thermal characteristics:

$1/\Delta T_n$ for particle potency and ΔT_{CS} for the amount of CS. Equation 1 embodies the Interdependence Theory with three terms representing three distances that contribute to grain size as illustrated by Figure 1. The first term is the amount of growth required to develop ΔT_{CS} equal to or greater than ΔT_n , the second term calculates the length of the diffusion field from the S-L interface to the end of the field where ΔT_{CS} is equal to ΔT_n and the third term is the distance from the end of the diffusion field to the next most potent (largest) particle.

$$d_{gs} = \frac{Dz\Delta T_n}{vQ} + \frac{4.6D}{v} \left(\frac{C_1^* - C_0}{C_1^*(1-k)} \right) + x_{sd} \quad [1]$$

where D is the diffusion rate of the solute in the liquid, v the initial growth rate of the solid-liquid (S-L) interface (which is closely related to the steady state growth rate, V), k is the partition coefficient and z is the proportion of CS that needs to be regenerated after the nucleation event. x_{CS} is calculated by the first term in Eq. 1 and the solute content (at% or wt%), c_0 , and that of the liquid at the interface, c_1^* , are used to calculate x'_{dl} by the second term (Figure 1). Q is the growth restriction factor, which will be defined in more detail later. Eq. 1 can be simplified to Eq. 2, highlighting the key factors that control the grain size [38]:

$$d_{gs} = \frac{5.6Dz\Delta T_n}{vQ} + x_{sd} \quad [2].$$

It is clear that CS is critically important in facilitating grain refinement of alloys and has been described recently in some detail [30]. It is very difficult, although not impossible, to obtain a fine-grained structure in a pure metal but is relatively easy in an alloy, and in general increased alloy content decreases the grain size [17, 43-46].

There are two key concepts that are important in understanding the role of solute on grain size that need to be considered:

1. Growth Restriction – the equations developed for dendritic growth show that the growth rate is inversely proportional to $mc_0(k-1)$ [32, 47-50]. This is the key reason for the reduction in grain size of the isothermal models [32, 33, 47, 51, 52] developed where there is a direct competition between nucleation where a higher ΔT_n is required to nucleate on less favorable particles, and the reduction in the rate of latent heat evolution through lower growth rates, which allows for a greater amount of supercooling to be generated.

2. Development of CS to facilitate nucleation – this recognizes the importance of the solute profile in front of the growing grain and the effect of the increased CS in front of the solid-liquid interface. It has been demonstrated by a number of authors [34, 53-55] that CS creates a region immediately in front of the interface where there is insufficient supercooling for nucleation to occur causing a nucleation free zone (NFZ).

The parameter that is used to quantify the effect that the solute has on the grain size is the growth restriction factor,

$$Q = \left| \frac{d(\Delta T)}{d.f_s} \right|_{f_s \rightarrow 0} \sim \sum_i m_i c_{0,i} (k_i - 1) \quad [3]$$

where m is the liquidus gradient, c_0 is the composition and k the partition coefficient for elements, i , in the alloy. Although there are a number of approaches to understanding this factor it is clear that thermodynamically it is related to the rate of development of CS at the beginning of solidification and is a simplification of the supersaturation parameters in an alloy [41]. The related supercooling parameter, $P = Q/k$ [41, 56] is also used but is understood to be less applicable in many situations. This has been discussed in detail elsewhere [41, 54, 56, 57].

From Equation 2 and Figure 2 [58], the grain size is linearly related to $1/Q$ when the particle number density is constant. It should be noted that recently it was proposed that a cube root relationship may fit the data better [59]. While this deals with the curvature sometimes observed when the data is plotted [60], a rapid reduction in grain size at very high Q-values has not been observed. Plotting the grain size against $1/Q$ is very informative for revealing the mechanisms by which grain refinement is occurring [57, 61-63].

Equations 1 & 2 have been validated against a wide range of Al alloy compositions [34]. It was also shown that plotting measured grain size data against $1/Q$ is a valuable method of determining the factors controlling the grain size of Mg [62, 64] and Ti [65] alloys even when values for the parameters in equation 1 are not known. Although equation 1 was developed for slow cooling, i.e. relatively quiescent melts with low temperature gradients, it has been shown to be a useful framework for evaluating the refinement of alloys in dynamic casting conditions such as high pressure die casting [66], welding [57] and when external fields [38, 63, 67, 68] are applied.

In developing equation 1 it was realized that nucleation will not occur within the diffusion field as the amount of CS is not at the maximum value and therefore insufficient for triggering nucleation on potent particles within this zone. As illustrated in Figure 1 the first two terms determine the size of the Nucleation-Free zone (NFZ). Shu et al [53] and Du & Li [55] also recognized that the diffusion field generated by CS suppresses nucleation within a region around a grain. As illustrated in Figure 2, it has been found [30, 34, 69] that NFZ can contribute more than 50% of the final grain size with the proportion decreasing for alloys with high Q values. Thus, a key strategy for reducing the grain size is to reduce the value of NFZ.

An important outstanding issue is to understand in more detail how elements interact with each other, i.e. how effective is the addition assumption described by Eq. 3. In many, if not most, cases the additive approximation (Eq. 3) is accurate [70, 71], particularly in dilute systems [41]. However, it is well documented that as the Si content increases in the Al-Si-Ti system the decreased partitioning of Ti reduces the Q-value [56, 72-74]. The additive approximation can also be less accurate in systems where a primary intermetallic such as Mg-Al-Mn is formed prior to solidification [73] or where a peritectic reaction occurs [41]. The improvement to computational thermodynamic models means that some of these effects can be more easily predicted [73]. Quested et al [41, 42] demonstrated that there is some deviation from linearity even in binary systems and that in multi-element systems deviation from linearity is related to the regular solution coefficient between the solutes. It should be noted that diffusivity is also assumed to be constant in Equations 1 & 2, and should be taken into account where there are distinct differences in diffusivity between elements, which are difficult to measure accurately [75-77].

3. Current understanding: the role of inoculation on grain refinement

Classical nucleation theory identifies the importance of heterogeneous substrates as a mechanism for reducing the free energy barrier to nucleation [78]. This is described by a wetting angle, which can be difficult to measure in practice for relatively potent nuclei. Hence, other models are required to describe the effectiveness of chemical inoculation, apart from direct grain size observation. There are two techniques that are usually used:

- measurement of the nucleation temperatures and/or re-calescence undercooling where a lower undercooling, ΔT_n , represents improved nucleation [13, 79-81]; and
- investigation of the crystallographic relationships between the nucleant particle and the alloy either experimentally [82-84] or theoretically [85, 86].

It is well recognised that there is a relationship between the measured undercooling and the crystallographic mismatch [81, 87, 88] and these are therefore complementary approaches.

Recently, there have been two important developments in our theoretical understanding of the crystallography of nucleation. The use of the edge-to-edge matching model [89], originally developed to explain solid-state phase transformations, has been particularly powerful in explaining the effectiveness of current grain refiners [90, 91]. Instead of considering only the misfit of atoms in close-packed planes as has been done [81, 87], the model proposes that the edges of the planes that meet at the interface should be close-packed or relatively close packed rows of atoms [89]. Consequently misfit between these edges and the associated planes can be determined to provide an indication of the potential of a substrate phase as a nucleant particle assuming that there is little or no surface energy anisotropy of either phase. Because the orientation relationships can be evaluated theoretically, many potential nucleant particles can be evaluated theoretically before trialing particles experimentally giving a greater chance of success. This approach sometimes identifies particles that are not thermodynamically stable [92] and therefore not appropriate. However, it has identified a number of particles that have proven to be particularly useful such as Al_2RE (RE= Rare Earth element) in many Mg-RE containing alloys [93-95].

Another recent promising approach is the use of epitaxial growth models to explain the early stages of nucleation [96], which builds on the earlier hypernucleation theory [97] and absorption theories of nucleation [98]. It is proposed that a pseudomorphic layer forms on the interface at a critical undercooling. The essence of the model is that as the solidification occurs a pseudomorphic layer with a structural resemblance to the substrate is formed at a critical undercooling. Misfit dislocations or other defects release strain energy if the lattice spacing is too dissimilar particularly as the layer thickness increases. To some extent this model confirms the importance of crystallography in the nucleation process but it goes a step further. Coupling this approach with the solute segregation model [25], solute elements can be identified

that assist the nucleation process by segregating to the interface reducing the interfacial energy barrier to nucleation. It is proposed that this could be the reason why some researchers have observed Al₃Ti layers on TiB₂ particles [19, 20, 23, 24, 99], possibly assisting nucleation, when from a simple understanding of the phase diagram Al₃Ti layers would not be expected to form as Al₃Ti is not thermodynamically stable at typical addition levels. Molecular dynamic simulations have indicated that ordering in the liquid phase where there is a low lattice misfit is to be expected [100]. Furthermore, these molecular dynamic simulations also indicate that TiB₂ particles may be more active if the close packed layer exposed to the Al melt contains Ti atoms rather than B atoms [101, 102].

Apart from crystallography, the size and morphology of the substrates are also important [103, 104]. There is a growing body of experimental evidence that particle size is important to nucleation [52, 64, 104, 105]. The equation that is used to describe nucleation on a flat substrate [33] is:

$$\Delta T_{fg} = \frac{4\sigma}{\Delta S_v \cdot d} \quad (4)$$

where σ is the interfacial free energy between the nucleant and the surrounding undercooled melt, ΔS_v is the entropy of fusion per unit volume of the solid and d is the diameter of the substrate.

Given that both ΔT_n (replaced by ΔT_{fg} in Equation 4) and the particle number density are critically important to the final grain size obtained there is a tradeoff between the two to obtain the finest grain size. Particles that are too large can also cause defects in forming operations. It appears that the particle size is optimally controlled between 1-5 μ m [52, 64, 106] in most systems, with particles less than 1 μ m being difficult to nucleate upon, and those larger than 5 μ m being too few to contribute substantially to nucleation density (unless it is a metal matrix composite [105]).

The optimum substrate size is related to the substrate morphology. For the same contact angle and the same critical radius, the classical models predict that nucleation is easiest on a concave substrate and most difficult on a convex substrate while nucleation on a flat substrate falls in between. Following Fletcher [107], the size effect of convex and concave substrates on nucleation has recently been analyzed in detail based on the classical models [108, 109]. Figure 4 summarizes the predictions. For nucleation on either a convex or a concave substrate, the size effect of the substrate is essentially limited to the cases when $R/r^* \leq 5$ (R: substrate radius; r^* :

critical radius) beyond which each substrate is effectively flat. Unlike flat substrates, the effect of the substrate size on grain nucleation is thus restricted to $\leq 5r^*$ for both convex and concave substrates.

When applying the free growth model, it is normally assumed that the nucleus forms on a flat substrate, be it a thin film or a spherical-cap although it has been extended to three dimensional surfaces [110]. Upon growth, the nucleus may pass through a hemispherical shape change during growth with the radius being equal to the half-length of the substrate. If size is not an impediment to nucleation then any particle provided by a master alloy is a potential nucleant. The particle density of added TiB_2 particles is very high in commercial practice, i.e. x_{sd} is very small (Equation 1). Thus adding more particles would be expected to only have a small effect on the grain size. Perhaps the size effect is important for very small particles but once a certain minimum particle size is reached a further increase in size does not affect the potency of the particles, which has been postulated previously including by the proponents of athermal nucleation in the Free Growth Model [103, 104]. More research is required to determine the most accurate description of a particle's potency.

Understanding of pre-nucleation ordering of atoms in the liquid phase prior to solidification has indicated that there are some similarities with spinodal decomposition and the formation of GP zones in solid state phase transformations [111]. It is proposed that alloying elements that lead to short range ordering in the liquid phase will assist nucleation and this has been observed in the addition of Cr to Al-Zn alloys [112] and in liquid gold alloys [113], both of which are face centred cubic (fcc) phases. It is proposed that a meta-stable icosahedral phase is formed upon which the stable phase nucleates, and then engulfs and transforms the meta-stable phase (Figure 5). Whilst further study is required to confirm such a mechanism, this could be another favorable factor for nucleation in peritectic systems on top of the role of growth restriction [17], crystallography [114, 115] and the driving force for nucleation [116].

4. Current Understanding: Physical processes

While inoculation is common practice in the metal casting industry it can also lead to several undesired by-products, including the formation of particle agglomerates, local defects, and impurities. Consequently, physical grain-refining processes, which are

free of the disadvantages of using inoculants, have continued to attract significant research interest. This is typically achieved through introducing an external form of energy to the liquid or semisolid state of the alloy at a certain level of frequency. The term 'dynamic solidification' has also been used to distinguish such solidification processes. One approach is to shear the melt either below [117, 118] or above the liquidus [119-122] to physically modify the solid or oxide particles. There has been some success with both of these approaches [123-126]. High intensity ultrasonic vibration and pulsed magneto-oscillation (PMO) are two such physical means whose grain-refining capabilities have been further examined over the last decade. These two approaches will be focused on here because in general they do not break up the melt surface and therefore avoid introducing further melt oxidation and gas absorption. In fact, ultrasonication has the beneficial effect of degassing the melt [127, 128]. Additionally, these processes have been applied to a wide range of alloy compositions which assists in revealing the active mechanisms of grain refinement.

Analyses of the literature data on ultrasonic grain refinement of magnesium alloys revealed that the Interdependence Theory applies to ultrasonic grain refinement of magnesium alloys from low to very high intensity levels (up to 1700 Wcm^{-2}) [38]. For a given level of applied ultrasonication intensity the resulting grain size (d) shows a clear linear relationship with $1/Q$ for both binary Mg-Al and Mg-Zn alloys (Figure 6) and commercial magnesium alloys [38, 129-131]. This result indicates that CS plays a critical role in ultrasonic grain refinement of magnesium alloys. On the other hand, it shows that the interdependence between growth and nucleation is preserved during solidification under high intensity (1700 Wcm^{-2}) vibrations applied at 20000 Hz. This has been confirmed by a recent experimental study of the effect of solute on ultrasonic grain refinement of magnesium alloys [132, 133]. It was found that high intensity ultrasonic vibration leads to significant grain refinement only in the presence of adequate solute. In addition, increasing the solute content as measured by the value of $1/Q$ can be more effective in grain size reduction than substantially increasing the ultrasonication intensity (beyond the cavitation threshold) [132]. The linear dependence of grain size on $1/Q$ or the Interdependence Theory was found to apply for ultrasonic grain refinement of magnesium alloys and aluminium alloys [63, 134].

It should be noted that in the absence of adequate solute, ultrasonication is still capable of refining magnesium and aluminium alloy grains, but the refinement is limited to a certain extent (e.g., $310 \mu\text{m}$ for pure magnesium) and also restricted to

areas close to the ultrasonication source [133]. In contrast, without ultrasonication, the alloys solidify as coarse-grained structures as nucleation is not able to interrupt the growth of the grains due to the large nucleation-free zone surrounding each nucleated crystal. The key role of ultrasonication is thus to create a sufficient number of nucleated crystals, which may include both fragmented crystals and those that nucleated on activated nucleating particles in the melt by ultrasonication. On this basis, the presence of adequate solute can enable nucleation upon growth of grains from close to the ultrasonication source to regions away from it, depending on the distribution of these nucleated crystals in the melt. Additionally, acoustic streaming facilitates a lowering of the temperature gradient which along with the induced convection enhances the transport and survival of grains throughout the melt [135]. Hence, significant ultrasonic grain refinement is a result of the combined effects of these developments.

Pulsed magneto-oscillation (PMO) is another potent physical grain-refining method, which can be applied to the solidification process of both non-ferrous and ferrous alloys [136-138]. Well-designed grain-refining experiments indicate that PMO refines the grain structure of pure aluminium through enhancing nucleation at or near the casting wall [137], assisted by the resulting uniform and lower temperature field in the melt which improves the survival rate of the dispersed wall crystals. Unlike ultrasonication, the PMO treatment changes the linear dependence of the grain size on $1/Q$ (Figure 7) [139]. The breakdown observed when $1/Q > 0.75$ implies that there was formation of an excessive amount of nucleated crystals due to PMO with respect to the solute present in the melt as measured by $1/Q$. The imbalance affected the interdependence between growth and nucleation. However, once adequate solute was present, for instance, when $1/Q < 0.3$, the linear dependence of the grain size on $1/Q$ prevailed. This, in fact, highlights the critical importance of solute in dictating the course of grain formation under the applied PMO treatment.

In general, solute plays an important role in other physical grain-refining processes too. The exceptions are when the nucleation rate or the number of crystallites produced by the physical approach is sufficiently high that the grain formation process evolves into an essentially nucleation or crystallite-generation controlled process.

5. Advanced experimental and analytical approaches.

Real-time solidification has been studied by several non-invasive techniques by Krujic et al [140] with the focus being on the study of the S/L interface – position, velocity and shape. These techniques included optical methods, X-ray radiography using high energy X-ray, ultrasound methods and eddy current detection. The synchrotron has the advantage over other non-invasive techniques in that several different aspects of solidification can be studied simultaneously [141]. For example, 2D X-ray radiography for the transient effects in solidification such as grain growth rates, columnar-to-equiaxed transition (CET), cell spacing and 3D tomography for studying the evolution of intermetallics and defect formation such as porosity and hot-tearing.

The use of the synchrotron has become the technique of choice to study in-situ real time solidification of metals [142]. Some areas of study conducted using these techniques are: CET [143], formation of equiaxed grains via solidification [144, 145] and columnar dendritic growth under the influence of fluid flow [146]. Since the Interdependence model predicts grain size based on the size and the growth rate of already nucleated and growing grains, the synchrotron technique offers the possibility to validate the assumptions behind the Interdependence model and alternative models through in-situ real time solidification study. Furthermore, the interdependence of growth and nucleation is supported by observations of waves of nucleation events as assumed by the Interdependence model [34] in grain-refined alloys. For example, real time solidification of Al-Si alloys, grain refined and unrefined, have been studied under the high-resolution BL20XU beamline at the Spring8 synchrotron facility [144, 147]. There was evidence of waves of nucleation events occurring in the grain-refined Al-4Si alloy. Similar studies were undertaken at the Diamond synchrotron on Al-Cu alloys which also reveals waves of nucleation events [148].

Furthermore, the growth rates of the growing grains can also be estimated by tracking the location of the dendrite tip in X-ray radiography studies. The measured values show that the magnitude of the average growth rate is very similar to that used in the Interdependence model [144]. Mathiesen et al [149] and Bogno et al [145] have shown growth rate fluctuations during the early stages of growth due to solutal interactions between neighbouring grains. This is an important area of study and more work is required in this area to definitively confirm the nature of the fluctuations and the relative contribution of thermal and solutal convection during the initial growth of a grain.

A substantial challenge for *in-situ* observation of solidification is that whilst the high resolution beam-line offers a 1 μm spacial resolution, the computer memory requirements to record a full solidification experiment are often a limiting factor compromising the data capturing frequency thereby degrading the time-resolution. The optimum spatio-temporal resolution required for studying the nucleation of grains and their subsequent growth poses a challenge. The image quality in alloy systems where only phase contrast is possible (e.g. Al-Si alloys) is also a challenge as the elements in the alloy being studied have similar atomic numbers. An option often used is to add Cu or focus on Al-Cu alloys [142, 146, 150], which increases the atomic number contrast, but Cu also affects the solidification path.

In-situ solidification studies have also led to the study of dendrite fragmentation. Dendrite fragmentation as an aid to increasing the number of grains and, therefore, grain refinement has been observed in some cases [150-153], and not reported in the others [144, 145]. It is likely that fragmentation occurs most commonly during directional solidification under particular conditions of low temperature gradient and a large solidification range [153], or in the case of equiaxed growth in the presence of an external field.

Synchrotron studies of solidification are still in their infancy and it is expected that our detailed understanding of solidification will be dramatically improved over the coming decade. To complement these studies there will be further improvements to the capability of numerical models and solidification simulation packages.

Numerical Modelling offers a unique way to test solidification theories and predict outcomes. Significant progress has been made both in terms of computational power and visualization. Using the computational power available a number of solidification theories have been confirmed, some are still to be confirmed, and others remain an open question [154].

Grain refinement in castings is essentially about grain nucleation and equiaxed growth of the nucleated grains. Any numerical model predicting the grain size must therefore take into account both events and needs to be coupled with a heat transfer model. However, the length scale of nucleation is significantly different from that for the growth of the S-L interface. Hence, while atomistic simulations are geared

towards studying nucleation [154], the models for predicting the solidification structure must use a different approach to tackling nucleation.

Numerical models for solidification typically employ a statistical approach based on the work of Rappaz [155] for modelling heterogeneous nucleation. Here nucleation is considered to be a continuous function of the undercooling (as opposed to a discrete function) assuming a Gaussian distribution. Once nucleation is triggered, one of the growth models is deployed (e.g. KGT model [156]).

The challenge for modelling nucleation is understanding the atomistic behavior during nucleation. Density functional theory and other atomistic models have made some progress, but more work is required in this area [100-102, 154, 157]. For instance, the effect of composition on the interfacial energy and its anisotropy are still not well studied although recent work suggests that the surface of TiB₂ particles is a more effective nucleation substrate when it is terminated by a titanium-rich layer rather than a boron-rich layer [101, 102]. Furthermore, atomistic models are considered to have provided new avenues to explore the free-growth theory [158]. Consequently, more work is required in this area.

6. Outstanding challenges

The Interdependence model shows why the Al-Ti-B master alloys for Al alloys and the Mg-Zr master alloy for some Mg alloys are so effective as both provide potent particles and solute with high growth restriction factors. Despite this knowledge and ongoing improvement to the cleanliness and efficiency of these master alloys, the greatest challenges in grain refinement are (i) attempting to increase the effectiveness of grain refining systems where only 1-2% of added particles [159, 160] act as heterogeneous nucleation sites; (ii) developing viable grain refinement methods for commercially important alloy systems where no potent grain refiners have as yet been identified; and (iii) understanding grain size control in emerging processing technologies such as additive manufacturing.

The first challenge poses these questions:

- how can the nucleation efficiency of the TiB₂ particles introduced to the melt be increased from around 1-2% to 10% or even to 50%; and

- how can we manage to further reduce the grain size of as-cast Al alloy billet products or castings from the current level down to less than 100 μm or even 50 μm by either chemical approaches and/or mechanical approaches.

There have been substantial improvements in the understanding of the reasons for the low efficiency of nucleant particle additions. One is the distribution of nucleant potencies where only the most potent nuclei act as effective sites [33, 106]. A further issue discussed in detail earlier is the presence of the NFZ due to the diffusion zone in front of the solid-liquid interface [34, 53, 55]. It is also clear that factors around nucleant morphology, e.g. surface curvature [108], the presence of poisoning elements [161], and the agglomeration of particles [162] affect refinement efficiency. It should also be noted that the low efficiency of the particle additions is an important quality issue too, where excess particles can lead to substantial problems in post-processing operations. From a grain refinement perspective, the $d - 1/Q$ relationship offers an innovative approach to the design of fine-grained cast alloys, namely high Q alloys. However, although the castability of alloys with high Q values tends to improve it does not improve in all cases [163]. Furthermore, mechanical properties of these high Q alloys may not be satisfactory, which need to be assessed on a case-by-case basis. Thus, all of the issues listed above need to be tackled to gain further refinement for a practical range of Q values.

There is a very good understanding of the role of solute grain refining through growth restriction and CS [32, 33, 50, 56], but it is apparent that through ready access to computational thermodynamic databases, the free energy driving force for a phase transformation (ΔG) may not always correlate directly with the supercooling, ΔT [41, 116]. Hence, the presence of some alloying elements may have a substantially greater effect on reducing ΔG . This is an area of study that could improve our ability to more accurately predict the grain size particularly in complex alloys.

Significant issues related to grain refinement remain for Al-Si, Mg-Al and Ti-based alloys.

One of the truly puzzling phenomena related to grain refinement is the grain size coarsening that occurs with Si additions above 2-3% [49, 164, 165]. Most commercial Al-Si foundry alloys are affected by poisoning so it is a practically important issue to address because a substantial reduction in grain size may improve the castability and properties of these alloys. The increase in grain size due to

poisoning is reproducible [49, 164, 166, 167], including *in-situ* synchrotron studies [144, 147] although the Si content at which the minimum grain size occurs appears to vary with solidification conditions [166]. The poisoning effect occurs with or without the addition of nucleant particles such as TiB₂ and without any Ti additions (Al typically contains 0.005Ti as an impurity) [166]. A recent study [168] indicates that the grain refining effect of an Al₃Ti₁B master alloy is not affected by Si poisoning of the nucleant particles. Rather, Si poisoning appears to affect one or more of the parameters in the first two terms of Equation 1. Molecular dynamic simulations [101, 102] that have demonstrated the importance of the Ti-layer in TiB₂ particles being exposed to the melt may also be able to assist in solving this issue. Understanding this problem may lead to a fundamental shift in our understanding of grain refinement and generate a new approach to improving grain refinement in many systems.

There have been efforts to develop new master alloys to overcome Si poisoning the most recent being the development of a Nb – B based grain refiner [169, 170] which is currently undergoing trials to test its commercial viability under the ExoMet program. ExoMet are also evaluating the ability of Al and Mg oxide particles to refine Al and Mg alloys [171].

In magnesium alloys, the greatest issue is to identify an effective commercially viable grain refiner for Mg-Al based alloys. There has been an extensive search for effective nucleant additions and some are relatively effective, particularly C-based grain refiners including C₂Cl₆ (although it is either banned or removed from use because of the toxic fumes emitted), Al₄C₃ or SiC which may actually form Al₂MgC₂ as the nucleant particle [172-176]. However, the further complication in Mg-Al alloys is the different phases arising from reaction with impurities or deliberate minor alloy additions, e.g. Mn, that form particles prior to the formation of α-Mg which may poison the nucleant particles [38, 62, 91, 177]. The most fruitful approach to identifying an effective grain refining system will need to address both of these issues.

Commercial titanium alloys are mostly wrought alloys with cast alloys only accounting for about 1-2% of the market. This is mainly due to melting and castability issues. Hence, grain refinement of titanium alloys has not received sufficient attention from the titanium industry. However, as the market slowly grows, there may be a need for a grain refinement technology in the future. In particular, a significant reduction in the as-cast grain size has the potential to enable direct hot rolling of as-

cast titanium alloy slab or ingot materials. This has recently been demonstrated on direct rolling of as-cast Ti-6Al-4V-0.1B (wt.%) ingots or slabs in which the addition of 0.1wt.%B produced an order of magnitude reduction in as-cast grain size of Ti-6Al-4V[178, 179].

Metal additive manufacturing (AM) processes are poised to transform the metal manufacturing industry, particularly in those areas where conventional manufacturing reaches its limitations in terms of both design freedom and manufacturing capabilities [180, 181]. AM of titanium alloys has been extensively studied, initially driven by the need to increase the 'fly-to-buy' ratio and to reduce the lead time in aircraft manufacturing. Additive manufacturing of metals is in essence a solidification processing based technology and although post manufacture heat treatments or hot-isostatic-pressing can be used to improve properties, it is most cost-effective to use parts as close as possible to the as-manufactured condition.

As yet grain refinement has not been regarded as an important issue that hinders the wider take-up of the process. However, in the case of the additive manufacturing of titanium alloys, there is noticeable anisotropy in the mechanical properties along different directions due largely to the formation of the columnar grain structures [182-184]. After hot isostatic pressing (HIP) or other post-heat treatments, the anisotropy can be reduced to an acceptable level [182-184]. If equiaxed grain structures can be achieved in the as-built state without noticeably changing the chemistry of the alloy, then that will mark a step forward in the microstructure control of the additively manufactured alloys. The key difference between solidification in AM and conventional casting technologies is that it involves the production of small melt pools (more similar to welding), and generates very high thermal gradients and cooling rates orders of magnitude higher than even high-pressure die casting. This leads to the development in turn of a very fine microstructure [185] and a tendency towards almost exclusively columnar growth particularly in Ti-based alloys [186-189]. While some advantages can be obtained in alloys with the more anisotropic behavior observed in alloys with a columnar grain morphology it is preferable that the grain structure can be engineered according to the requirements of the application [190]. This may reduce or eliminate the need for post-processing such as hot isostatic pressing or other heat treatments.

To engineer the microstructure in AM the physics of the solidification process is required to be understood in some detail. Increased growth velocity, V , decreases

the size of the solute diffusion field in front of the growing grain. It appears that this is the reason for much of the grain refinement observed with increased cooling rate [49, 60, 191] for relatively moderate cooling rates up to 20K/s.

The other factor that is important is the increase in the temperature gradient (Figure 8) [192], which is likely to be more influential at much higher cooling rates. This has at least two effects. One is that the distance to the point of maximum supercooling (CS zone, CSZ) decreases, which would tend to decrease the grain size (Figure 9 (a)). The other is that the magnitude of the supercooling reduces which would be predicted to increase the grain size and in extreme cases suppress nucleation entirely leading to columnar growth (Figure 9(b)). It is likely that this is contributing to the predominantly columnar structures found in AM. Further factors that need to be considered are the possibility of greater thermal supercooling (TS) and how that affects nucleation and growth (TS is often neglected as it is small compared with CS) and the role of subsequent re-melting or partial re-melting of prior solidified layers during subsequent passes.

To date little investigation has been undertaken into additive manufacturing and its effect on the grain size and formation but it is apparent that current grain refinement theory will be able to assist with understanding how to engineer grain structures in this process.

7. Summary

A review of recent developments in our understanding of the mechanisms and methods of producing a fine grain size show that considerable advances have been made over the last fifteen years particularly in understanding the interdependence of nucleation and growth in obtaining fine grain sizes. New tools such as Synchrotron real-time x-ray observations have also been developed to study the full solidification pathway from nucleation to the fully solidified microstructure. The grain size - $1/Q$ relationship offers an innovative approach to revealing the mechanisms of grain refinement and for the design of fine-grained cast alloys, namely high Q alloys. A nucleation free zone has been identified as part of the reason for the limited effectiveness of nucleant particle additions. More detailed knowledge of the nature of interfaces for nucleation is being developed using epitaxial growth models and molecular dynamics calculations. However, there are still many challenges to be overcome in order to effectively refine Mg and Ti alloys and improve the

effectiveness of master alloys for Al alloys. There has been an increased interest in physical approaches, such as ultrasonics and pulsed magneto-oscillation, on grain refinement and many of these approaches show promise. However, there are practical hurdles to reliable implementation in a commercial foundry environment casting complex shapes. Additive manufacturing is providing a challenge for obtaining equiaxed grained structures and is likely to be an important area of research in the near future.

Acknowledgements

The authors acknowledge support from ARC Discovery Projects DP120101672, DP140100702 and Linkage Project LP150100950 and the ExoMet Project co-funded by the European Commission's 7th Framework Programme (contract FP7-NMP3-LA-2012-280421), by the European Space Agency and by the individual partner organisations.

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Figures

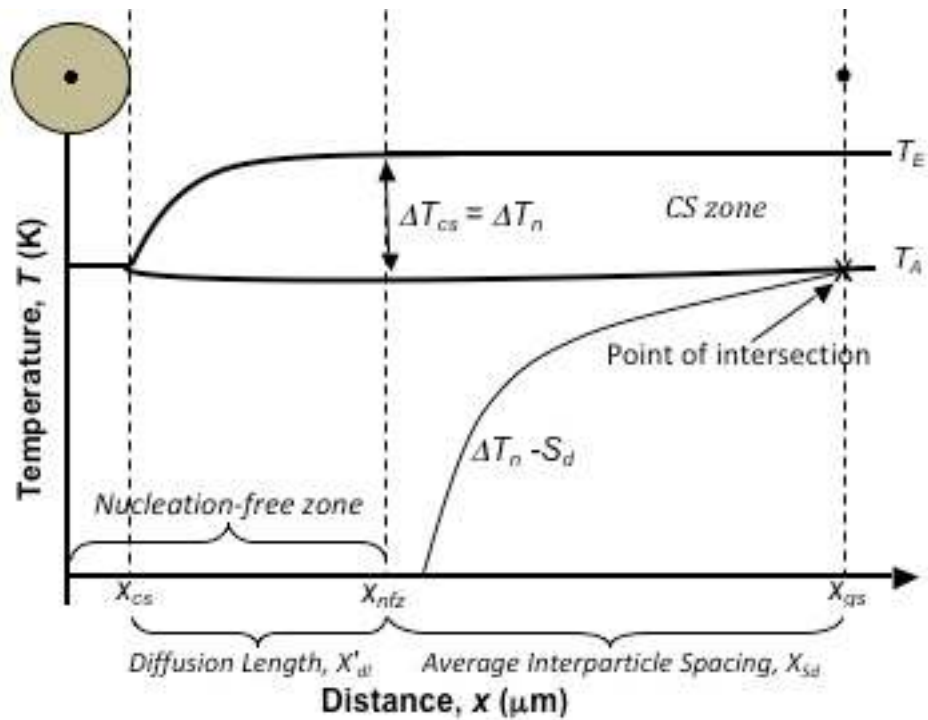


Figure 1. Schematic representation showing the intersection between the actual temperature T_A and the $\Delta T_n - S_d$ curve indicating the location of the nucleation event, and the three regions that together establish the grain size of the microstructure: x_{cs} , x'_{dl} and x_{sd} . The first two regions x_{cs} and x'_{dl} together represent a nucleation-free zone where nucleation is not possible for the particle size and potency ($1/\Delta T_n$) distribution described by $\Delta T_n - S_d$ [34].

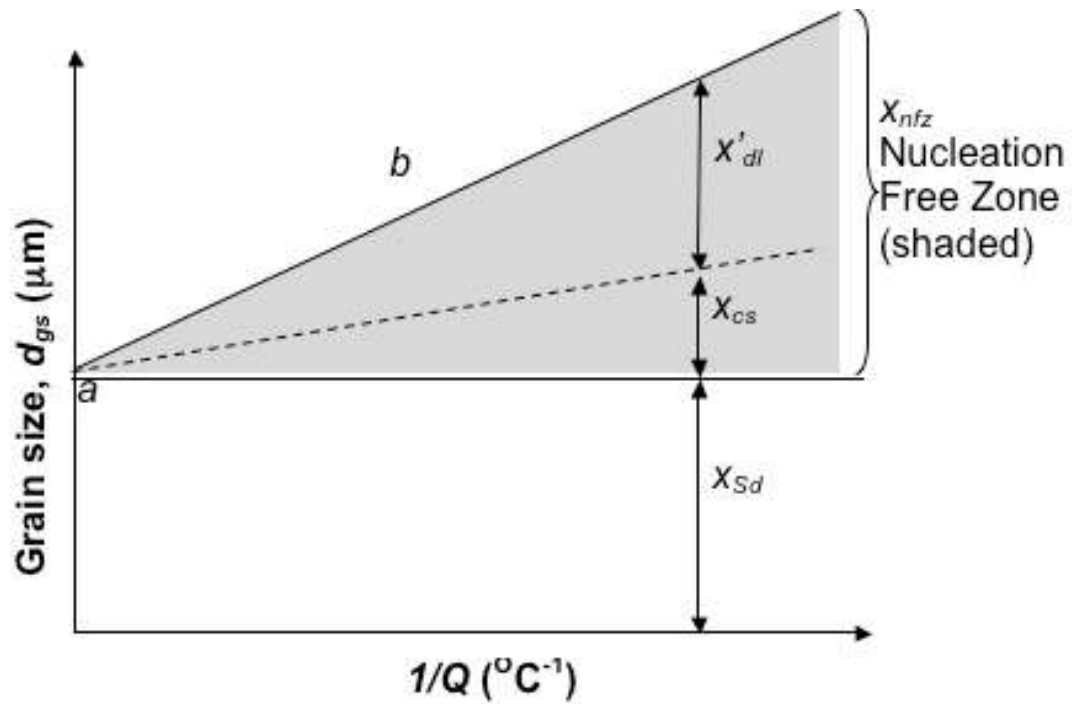


Figure 2. A simple representation illustrating that for each value of Q the grain size is the result of three components: x_{Sd} is the average distance to the activated particles and b is equal to the gradient of x_{CS} plus x'_{dl} over a unit of $1/Q$ (Eqn. 2). x_{Sd} is a constant when the particle number density is constant [58].

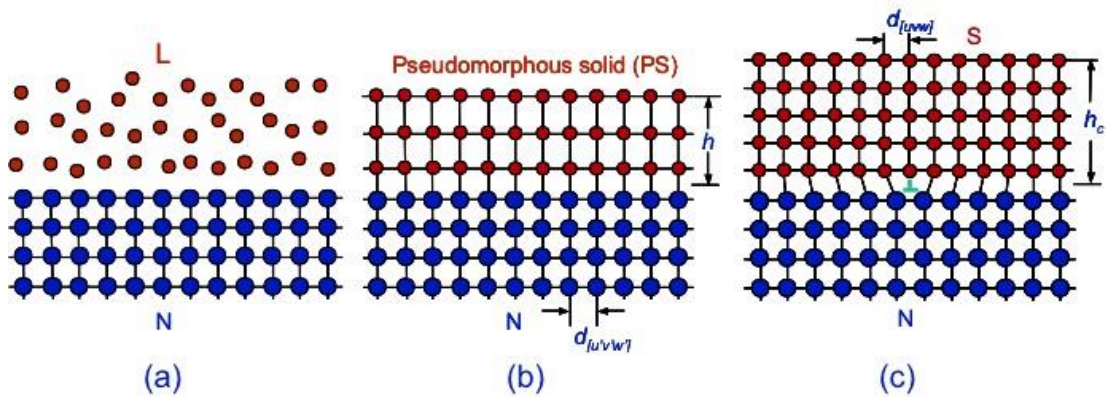
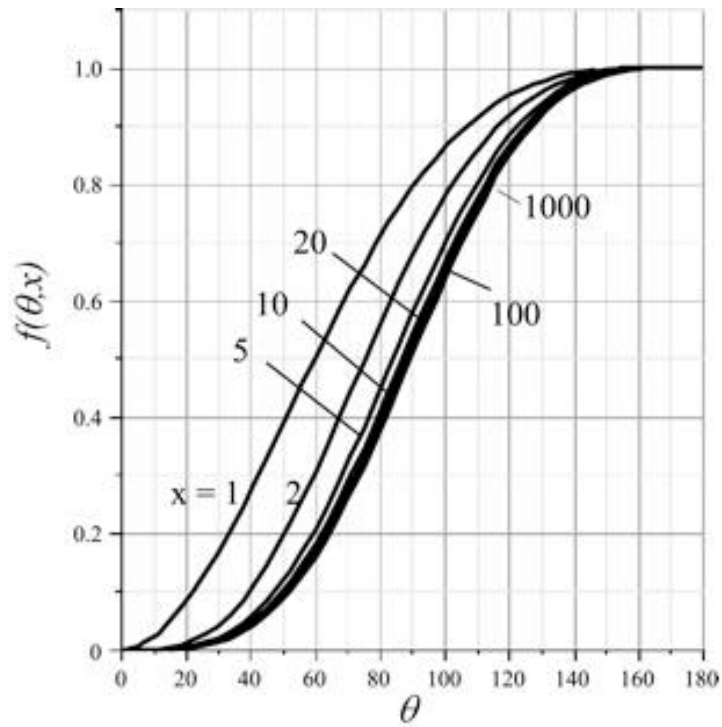
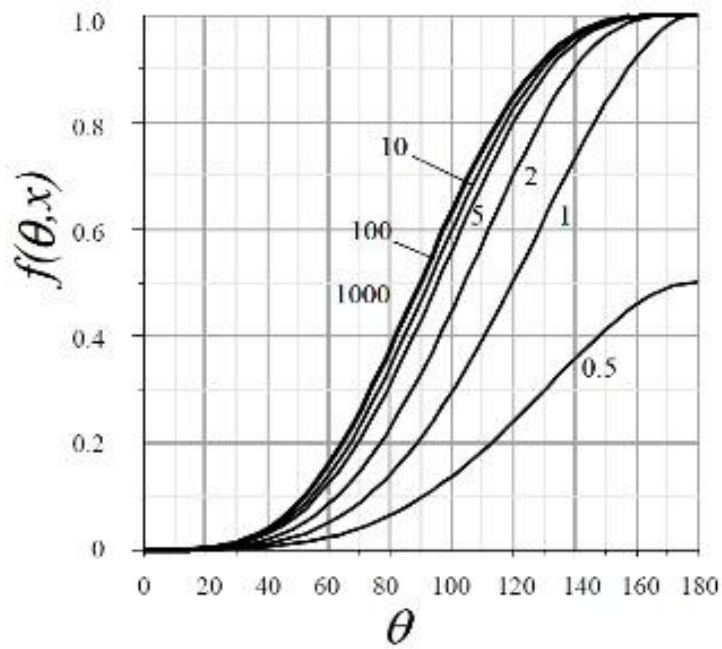


Figure 3. Schematic illustration of the epitaxial model for heterogeneous nucleation of a solid phase (S) on a potent nucleating substrate (N) from a liquid phase (L) under $\Delta T > \Delta T_c$: (a) sketch showing the L/N interface before the growth of the PS layer ($h = 0$); (b) the initial formation of the pseudomorphic solid (PS) with a coherent PS/N interface; and (c) completion of the epitaxial nucleation at a critical thickness (h_c) by creation of misfit dislocations at the S/N interface to change the PS layer into the solid and to convert the coherent PS/N interface to a semicoherent S/N interface [96].



(a)



(b)

Figure 4. The shape factor $f(\theta, x)$ is plotted against the contact angle θ with respect to different values of $x=R/r^*$ (ratio of substrate radius, R , and critical radius, r^*), to show (a) effect of the convex (spherical) substrate size and (b) effect of the concave (spherical) substrate size on heterogeneous nucleation. Reproduced from Refs [108, 109].

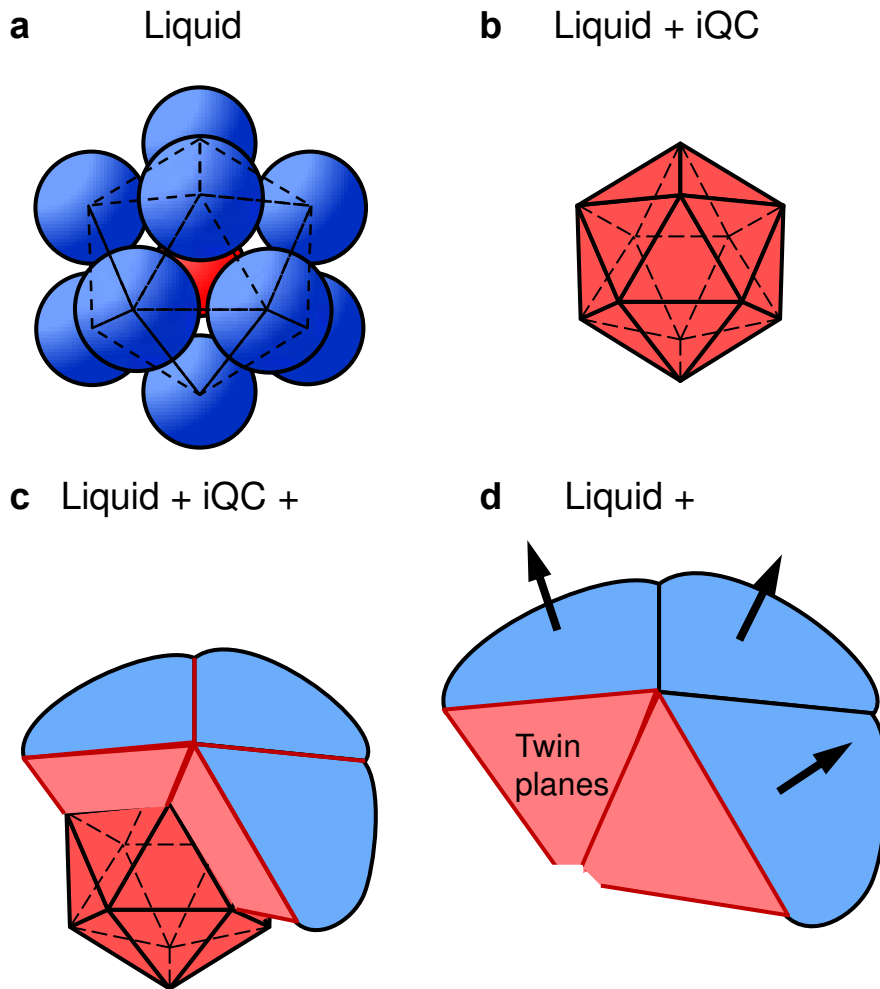


Figure 5. The stages of nucleation in an Al-Zn:Cr system as proposed by Rappaz & Kurtuldu [111]. (a) The blue Al and Zn atoms form a short range ordered clusters with the red Cr atoms. (b) The icosahedral phase forms in the liquid. (c) The α -fcc phase forms on the icosahedral facets. (d) The fcc phase grows and dissolves the icosahedral phase due to the peritectic nature of the phase diagram.

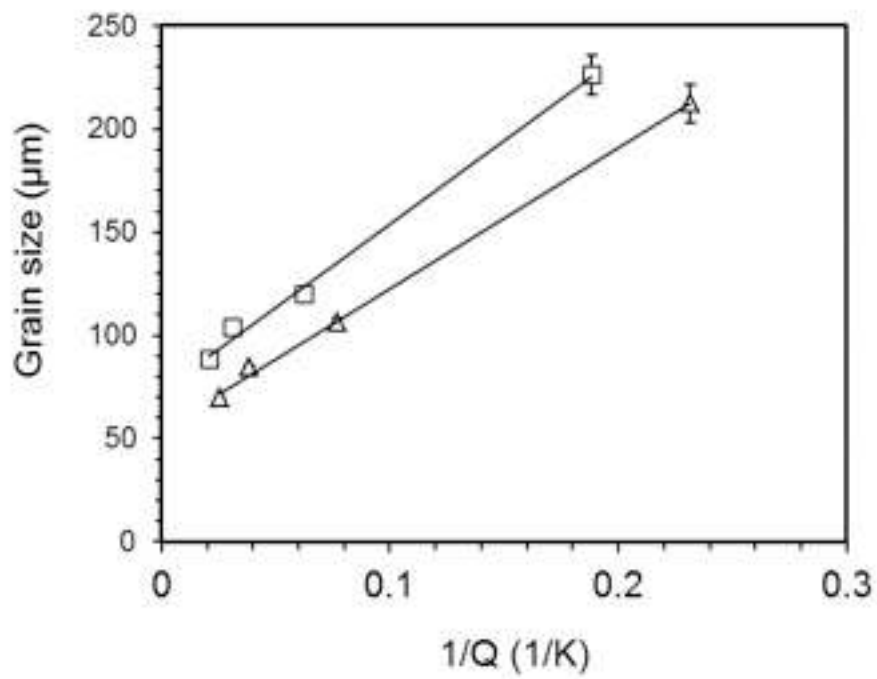


Figure 6. The linear dependence of grain size on $1/Q$ for high intensity ultrasonic grain refinement of binary Mg-Al (squares) and Mg-Zn (triangles) alloys. Reproduced from Ref. [131]

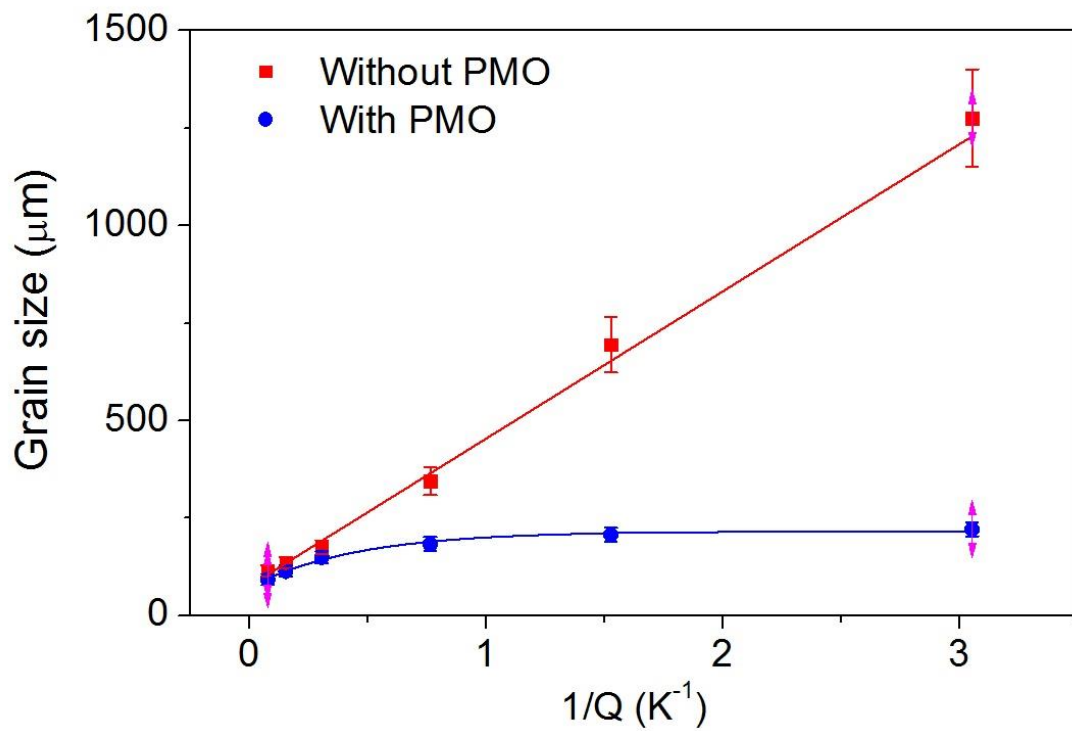


Figure 7. The variation of grain size with $1/Q$ for pure Al inoculated with different additions of an Al_3Ti_1B master alloy with and without the application of pulsed magneto-oscillation (PMO). Reproduced from Ref [139].

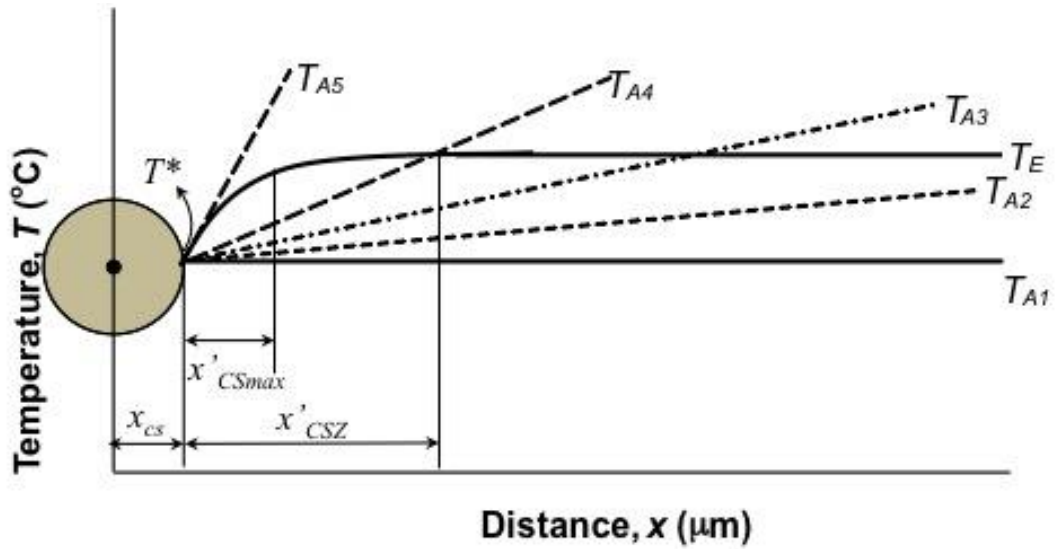
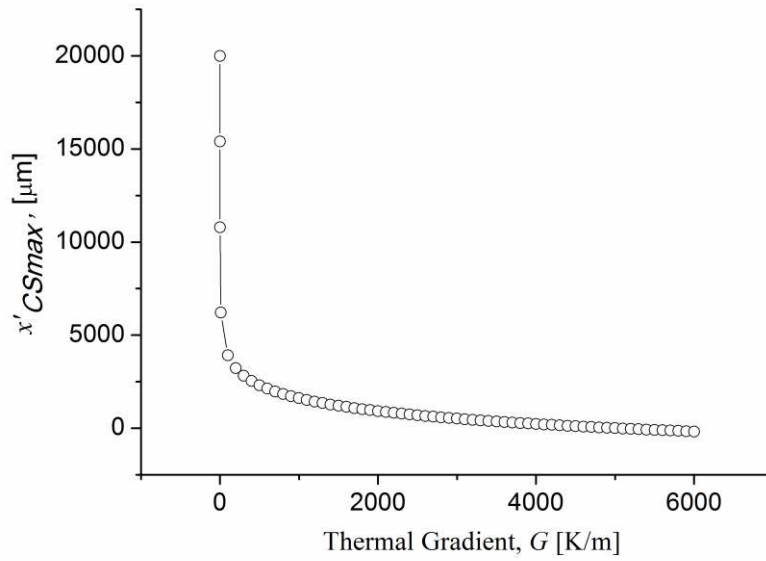
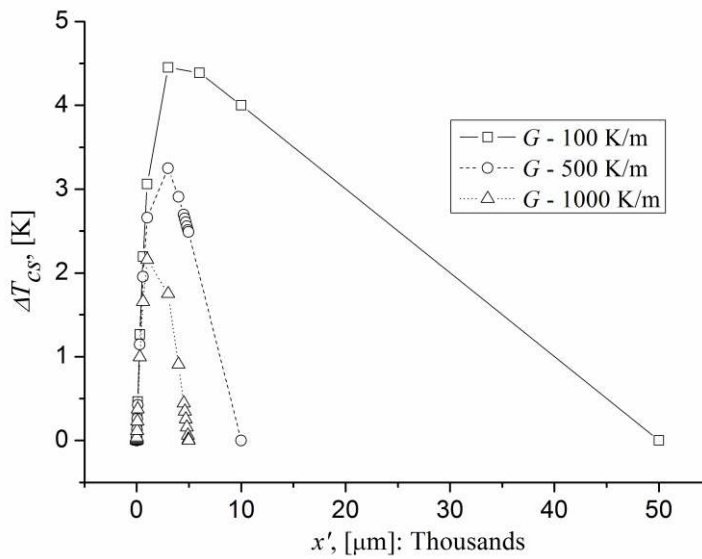


Figure 8. Schematic representation of the constitutionally supercooled zone (CSZ) as described by the Interdependence model with varying degrees of thermal gradient denoted by T_{A1} - T_{A5} . The approximate lengths of the distance of the CSZ, x'_{CSZ} (where ΔT_{CS} is positive), and the distance from the solid-liquid interface to maximum supercooling, x'_{CSmax} (corresponding to ΔT_{CSmax}) for T_{A4} are also shown in the figure. Reproduced from Ref [192].



(a)



(b)

Figure 9. (a) The distance x'_{CSmax} , from the solid-liquid interface to the maximum supercooling ΔT_{CSmax} , shown as a function of thermal gradient. At high thermal gradients, G , x'_{CSmax} approaches zero. (b) The constitutional supercooling, ΔT_{CS} ($= T_E(x') - T_A(x')$) as a function of distance, x' , for different G . As G increases x'_{CSZ} , the total distance of positive ΔT_{CS} , and ΔT_{CSmax} decrease. Reproduced from Ref [192].

The key developments related to the papers with * or ** are described below:

1. Identification and understanding of the nucleation free zone (References 30, 55, 69)
2. Developing an understanding of epitaxial nucleation in these alloys, and the molecular dynamic simulations of nucleation showing the importance of the chemistry of the melt facing lattice plane on nucleation (25, 96, 100, 102)
3. The use of synchrotron observations in observing grain refinement (144, 145, 147, 150)
3. Understanding the use of external fields on nucleation phenomena work (57, 127, 128, 138, 139, 185)
4. The development of a new grain refiner (Al-Nb-B) for grain refining Al-Si alloys (169, 170) and oxide based grain refiners (171).
5. New understanding of the role of peritectics related to free energy driving force and pre-nucleation (17, 111, 112, 113, 116)