Recent advances in grain refinement of light metals and alloys

M.A. Easton [a,*], M. Qian [a], A. Prasad [b], D.H. StJohn [b]

[a] RMIT University, School of Aerospace, Mechanical and Manufacturing Engineering, Melbourne, VIC 3001, Australia
[b] Centre for Advanced Materials Processing and Manufacturing (AMPAM), School of Mechanical and Mining Engineering, The University of Queensland, St Lucia, QLD 4072, Australia

ARTICLE INFO

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 are presented.

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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

* Corresponding author.
   E-mail addresses: mark.easton@rmit.edu.au (M.A. Easton), ma.qian@rmit.edu.au (M. Qian), aprasad3@uq.edu.au (A. Prasad), d.stjohn@uq.edu.au (D.H. StJohn).

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. Eq. (1) embodies the Interdependence Theory with three terms representing three distances that contribute to grain size as illustrated by Fig. 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, x_{sd}, is the distance from the end of the diffusion field to the next most potent (largest) particle.

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

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_l^*, are used to calculate x'_{dl} by the second term (Fig. 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]:

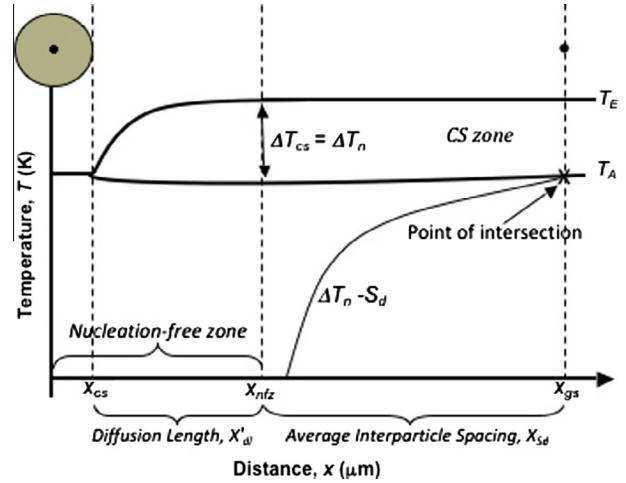$$d_{gs} = \frac{5.6Dz\Delta T_n}{vQ} + x_{sd}. \qquad (2)$$

Fig. 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].

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,

$$Q = \left|\frac{d(\Delta T)}{d.f_s}\right|_{fs \to 0} \sim \sum_i m_i c_{0,1}(k_i - 1) \qquad (3)$$

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].