Heterogeneous nucleation on potent spherical substrates during solidification

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Abstract

For a spherical-cap nucleus to become a “transformation nucleus”, the linear dimension \(d\) of the flat substrate must exceed the critical nucleus size \(2r^*\). This Turnbull criterion \((d > 2r^*)\) defines a minimum undercooling for grain formation on, and effective inoculation with, flat nucleating substrates. However, for nucleation on potent substrates the spherical-cap model is no longer tenable. The free growth model has in general considered the growth of a two-dimensional nucleus on a potent flat substrate. Inspired by the particle-core structures observed in magnesium alloys after inoculation with nearly spherical zirconium particles, a model has been proposed, on the basis of an adsorption and surface diffusion mechanism, for heterogeneous nucleation and grain formation on potent spherical substrates of \(d > 2r^*\). The critical undercooling required is found to be approximately the same as that defined by Turnbull’s patch nucleation theory. The model shows excellent agreement with experiments compared from different perspectives.

Keywords: Heterogeneous nucleation; Transformation nucleus; Inoculation; Grain refinement; Adsorption

1. Introduction

The initiation of a phase change to a more condensed state on the surface of a substrate is a problem of broad scientific interest and technological importance. The ability to control such a process lies at the heart of the development of a novel technology or microstructure [1]. This is because nucleation controls to a large extent the initial structure type, size scale and spatial distribution of the product phases [2]. In the metal casting industry, for instance, it is common practice to introduce nucleating agents to a liquid metal, referred to as inoculation, for the formation of fine, uniform and equiaxed non-dendritic grains. In fact, the process is so important that, without effective inoculation, many cast alloys will have much reduced commercial values. Magnesium alloys that are developed on the exceptional grain-refining ability of zirconium and aluminium alloys that are based on inoculation with the Al–Ti–B-type master alloys are typical examples in this regard.

Because of its obvious importance, many models have been proposed for heterogeneous nucleation on substrates of different potency (measured by the contact angle \(\theta\) [3]) and geometries. This work is concerned with heterogeneous nucleation and grain formation on potent spherical substrates during solidification, inspired by observations of the grain structures in magnesium alloys obtained after inoculation with nearly spherical Zr particles. The purpose is to develop a thermodynamic criterion for effective inoculation with potent spherical substrates.

2. Theoretical background

2.1. The classical models and Turnbull’s patch nucleation theory

Heterogeneous nucleation may be regarded as a “geometrical concept” [4] in that the process is significantly affected by the geometry of the substrate. In the classical flat substrate model [5], in order to be able to accommodate a spherical-cap nucleus, the minimum substrate surface and
dimension \( (d) \) need to satisfy \( \pi (r^* \sin \theta)^2 \) and \( 2r^* \sin \theta \), respectively (Fig. 1a), where \( r^* \) is the critical nucleus radius. Since \( 2r^* \sin \theta < 2r^* \), in principle, a flat substrate with a linear dimension \( (d) \) in the range \( 2r^* \sin \theta < d < 2r^* \) can still act as a nucleating substrate. However, the nucleus thus formed will not be able to grow into a grain [3]. Turnbull [3] referred to such flat substrates and those that are slightly larger than \( 2r^* \) as patches. He established that, when \( d > 2r^* \), any nucleus formed on the patch surfaces with a radius larger than \( 2r^* \) will be able to become a transformation nucleus. That is, it will grow on the surface to a dimension exceeding \( 2r^* \) and thence into the body of the supercooled liquid to become a grain. However, when \( d < 2r^* \), crystal nuclei formed on the patch surfaces can still grow to the patch boundary but they will not, in general, be able to become transformation nuclei [3]. This is because any further growth in the direction perpendicular to the surface will decrease the radius of curvature of the crystal. This exerts a barrier to growth [6].

The critical condition is when \( d = 2r^* \). Substituting the expression of \( r^* \) gives

\[
d = \frac{4\gamma_{SL}T_m}{L_v \Delta T}
\]

where \( \gamma_{SL} \) is the interfacial energy, \( T_m \) the melting point, \( L_v \) the latent heat of fusion per unit volume of the crystal and \( \Delta T \) the undercooling. Eq. (1) defines a minimum undercooling \( (\Delta T_{\text{min}}) \) for the formation of a transformation nucleus or a grain on a flat substrate. It also gives exactly the same criterion for the free growth model [6]. However, apart from assuming a spherical-cap nucleus, the free growth model has further considered the growth of a two-dimensional nucleus on a flat substrate [6]. This somehow extends the applicability of Eq. (1) to nucleation on potent flat substrates, where the spherical-cap assumption breaks down, as will be elaborated subsequently.

![Fig. 1. Various models proposed for heterogeneous and grain formation on substrates of different potency and geometries: (a) the flat substrate model and Turnbull’s patch nucleation model, drawn on the basis of Turnbull’s description [3], where for a spherical-cap nucleus to become a transformation nucleus, the linear dimension \( (d) \) of the substrate must exceed \( 2r^* \); (b) Fletcher’s convex substrate model, redrawn according to Ref. [7]; (c) the concave substrate model, redrawn according to Ref. [9]; (d) Sundquist’s model [13], where the nucleus is proposed as an adsorbed layer of atoms on the surface of a potent flat substrate, drawn according to the description given in Refs. [9, 13]; (e) a schematic of the M–H model (see the text for details), drawn according to Maxwell and Hellawell’s description [18]; (f) liquid film/drop formation on a solid wettable spherical particle [20], where the nucleus is treated as a uniform layer of liquid film enveloping the particle, redrawn according to Fig. 1 of Ref. [20].](image-url)
Fletcher [7] considered heterogeneous nucleation on convex substrates (Fig. 1b) using the classical approach, and discussed the size effect of the substrate through a shape factor \( f(m, x) \)

\[
f(m, x) = 1 + \left( \frac{1 - mx}{g} \right)^3 + x^3 \left\{ 2 - 3 \left( \frac{x - m}{g} \right) + \left( \frac{x - m}{g} \right)^3 \right\} + 3mx^2 \left( \frac{x - m}{g} - 1 \right)
\]

in which \( m = \cos \theta, x = R_p/r^*, \) where \( R_p \) is the substrate radius (\( R_p > r^* \)), and \( g = (x^2 - 2mx + 1)^{1/2} \). The minimum substrate size to be able to accommodate a spherical-cap nucleus is defined by \( R_{\text{min}} = r^* \sin \psi/\sin \phi \), where \( \psi = \theta + \phi \). For given \( \theta \) and \( r^* \), Fletcher’s model predicts that \( f(m, x) \) decreases with increasing \( R_p \). That is, large spherical substrates are thermodynamically more favourable as nucleating substrates compared with small ones.

Nucleation can also occur on a concave substrate (Fig. 1c), or on the surface of a pit or crack in a flat or convex substrate [8–10]. The geometrical factors generally play a more important role in such cases. For example, nucleation may occur on the surface of a crack even if \( \theta \) is nearly 90° [10]. For given \( \theta \) and \( r^* \), nucleation occurs most readily on concave substrates [9]. However, since such nucleation accounts for only a small part in an inoculated melt, they are often ignored in practice.

2.2. Nucleation on potent substrates by adsorption

An important assumption embedded in the classical approach is the use of a spherical-cap nucleus. This has been an issue of considerable controversy when \( r^* \) or \( \theta \) is very small or when both \( r^* \) and \( \theta \) are small. Yang and co-workers [11] in 1954 used the classical approach to consider the formation of thin metal (sodium) films by condensation of the sodium vapour on different substrates. They found that the calculated critical nucleus size (2\( r^* \)) from the experimental data is just about the size of a unit cell of sodium, which contains nine atoms. This gives an idea about how small a metal nucleus could be. Having noticed this, Walton [12] remarked that for nuclei of this magnitude the uncertainties concerned with the spherical-cap model and the concept of surface energy become serious, because the critical nucleus approaches atomic dimensions or is actually planar under such circumstances. The concept of \( \theta \) no longer applies. In addition, with such small numbers of atoms significant changes in the structure of the nucleus will occur with changing size [12]. Walton then considered the formation of thin metal films through the use of the partition function and kinetic theory on the basis of an adsorption mechanism, followed by atomic rearrangement to achieve a preferred configuration (i.e. having the highest binding energy). Walton’s approach avoided the use of both the spherical-cap assumption and the concept of surface energy.

Sundquist [13] in 1962 considered heterogeneous nucleation in the solidification of tin at low supercooling (implying a small \( \theta \)), and pointed out that the spherical-cap assumption is no longer tenable in such cases. He proposed that the nucleus formed at low supercooling should be treated as “a monolayer of (tin) atoms occupying the atomic sites on the catalyst surface” (Fig. 1d), and derived an expression for the nucleation rate to re-explain the reported experimental observations. On this basis, Chalmers [9] in 1964 made the following remarks about nucleation on potent substrates:

A monolayer of atoms on the surface of a substrate cannot be regarded as a group of atoms brought together by a fluctuation in the liquid; it is more reasonable to regard it as an adsorbed layer in which the atoms can be arranged in many ways. The groupings of the atoms in the adsorbed layer play the same part as the embryo in the liquid; some have the structure of the crystal and, if large enough, can provide the starting point for further growth.

These important remarks did not receive the attention they deserved in the past. Recently, evidence in favour of the adsorption mechanism has been uncovered using high-resolution transmission electron microscopy. These include Si nucleation by a monolayer of catalytic AlP on Al crystals in Al–Si–P alloys and Al nucleation by a monolayer of catalytic TiAl3 on TiB2 substrates in Al-based glasses [14]. In addition, the role of adsorption in nucleation on wettable particles in non-metallic systems has been investigated using the density functional theory [15], self-consistent field theory [16] and computer simulations [17]. It is shown that substrates that preferentially adsorb the nucleating species favour nucleation, and for sufficiently strong adsorption nucleation could become barrierless [16]. In general, adsorption has become an accepted mechanism for nucleation on potent/wettable substrates.

2.3. Nucleation on potent substrates by wetting

In an attempt to understand the grain refinement observed in Al–Ti and Al–Zr alloys (low supercooling, <2 °C), Maxwell and Hellawell [18] proposed a mechanism that combines the spherical-cap model with wetting for grain formation on faceted Al3Ti or Al3Zr particles (the M–H model). They assumed that, after a spherical-cap nucleus forms on a facet of an Al3Ti or Al3Zr particle, that particle will be immediately enveloped in aluminum (Fig. 1e), due to efficient wetting implied in the small undercooling, which implies a small \( \theta \). This leads to a spherical envelope, whose radius was assumed to be approximately equal to the dimensions of the particle. This is compatible with the critical nucleus size of aluminium at low supercooling compared with the size of the intermetallic particle [18]. Subsequent growth of the spherical envelope was described as a function of the melt supercooling using a spherical growth model. As has been well documented, the many discoveries made out of the M–H model have profoundly improved our understanding of inoculation.
A unique feature of the M–H model is that although classical nucleation is assumed, the actual ‘effective’ nucleus is that zero-thickness spherical envelope of aluminum formed by efficient wetting.

In fact, wetting as a mechanism for nucleation has long been presumed in the condensation of vapour on wettable insoluble particles [19–21], where the nucleus is often assumed as a uniform liquid film (Fig. 1f). The work of formation for such a nucleus has been treated differently depending upon the thickness of the liquid film. For a thin liquid film, it has been suggested that the work of formation should include an additional term to reflect the interactions of the surface forces between the substrate and nucleus [20]. This additional term exhibits a power-law dependence on the thickness of the film and cannot be reduced to the “volume” and “surface” terms in the work of formation for a thick liquid film [20], where the additional term is negligible due to the increased thickness.

In summary, both adsorption and wetting have been treated as a mechanism for nucleation on potent/wettable substrates. However, it should be pointed out that, when considering nucleation in atomic dimensions, adsorption is a more functional mechanism than wetting. This is because liquids do not spread down to monolayer dimensions due to the effect of long-range interactions [22]. In contrast, adsorption can always result in a nucleus of monolayer dimensions.

3. Model development

The height ($h$) of a spherical-cap nucleus on a flat substrate is given by $r^*(1 - \cos \theta)$, which decreases rapidly with decreasing $\theta$. For example, $h \leq 0.06 r^*$ when $\theta \leq 20^\circ$. Therefore, for a small $r^*$, which implies a large $\Delta T$ in most cases, $h$ can readily approach atomic dimensions for substrates of $\theta \leq 20^\circ$ [14] or even $\theta \leq 30^\circ$ [23]. This is well before complete wetting is achieved [23]. This means that all classical models that assume a spherical-cap nucleus will generally break down for nucleation on substrates of $\theta \leq 20^\circ$, which are often of interest in practice. It is desirable and necessary then to re-examine the nucleation on such substrates. The free growth model [6] has in general considered the growth of a two-dimensional nucleus on a potent flat substrate as an alternative mechanism for grain formation. The model presented below focuses on nucleation and grain formation on potent spherical substrates during solidification.

The problem was inspired by the characteristic Zr particle-core structures [24, 25], shown in Fig. 2a and b, observed in magnesium alloys inoculated with nearly spherical Zr particles (Fig. 2c). Zr and Mg have the same type of crystal structure and almost identical lattice constants [26]. In addition, solutal Zr has a strong growth restriction effect on Mg [27]. These factors make Zr a nearly perfect grain refiner for Mg [28, 29]. From a wetting point of view, because of the very similar crystallographic characteristics, it is reasonable to assume that nearly com-

Fig. 2. Backscattered electron (BSE) micrographs showing (a) the characteristic zirconium particle-core structures in magnesium inoculated with 1%Zr and solidified at a cooling rate of ~0.6 °C/s; (b) an enlarged view of a particle-core structure; (c) the nearly spherical Zr particles in a Mg–33.3%Zr master alloy used for inoculation. The bright particles at the centre of the cores in (a) are almost pure Zr particles, which are the nucleants for the outside cores, i.e. the halos, which contain 1–3%Zr, while the dark areas are virtually zirconium free.
plete wetting occurs on all crystalline faces of the Zr substrate exposed to molten Mg. This differs from the case between TiB₂ and molten Al, where Al seems to crystallize only on the {0001} basal faces of TiB₂ [6]. The bright particles at the centre of the cores in Fig. 2a and b are nearly pure Zr [24]. They are the nucleants for the outside magnesium cores, i.e. the halos, which contain 1–3%Zr [24]. The dark regions are matrix magnesium grains solidified from the liquid that is depleted of dissolved Zr in the late stage of solidification. The Zr particle-core structures can form when the Zr content is either above or below the peritectic composition [24,30].

Following Kim and Cantor [31], we assume that the sharp onset of interface properties, the crystal will grow spherically until a critical size is reached [29,33]. The critical undercooling for the sharp onset of interface adsorption is determined below.

Fig. 3 schematically shows a model proposed for nucleation and grain formation on a potent spherical particle of radius \( r_p \) \((r_p \geq r^* )\) in a supercooled liquid metal. The primary assumptions employed are as follows: (i) isotropy of interface properties; (ii) nearly complete wetting (small \( \theta \)); and (iii) the spherical substrate having an identical environment in the melt at all points on its surface. With increasing undercooling, i.e. the driving force for nucleation, it is assumed that the atoms from the liquid at the interface will become adsorbed on the substrate surface to occupy the atomic sites available there. Following Kim and Cantor [31], we assume that the sharp onset of interface adsorption corresponds to the surface of the substrate acting as a catalyst for nucleation when a critical undercooling is achieved. Also, we assume that the adsorption ends up with a continuous thin layer of atoms enveloping the substrate surface due to assumption (iii). Owing to the high mobility of the solidifying atoms at low undercooling \((\leq 5 \, ^\circ C)\) for large masses of liquid metals that crystallize to close packed structures [32], the atoms in the adsorbed layer can be arranged in many ways, as suggested by Chalmers [9], through surface diffusion. One of them is that typical of a crystal structure. Once this occurs at a critical \( \Delta T \), it is reasonable to assume that heterogeneous nucleation has occurred. Because \( r_P \geq r^* \), subsequent growth will occur spontaneously in the supercooled liquid, leading to the formation of a grain. Under the assumption of isotropic interface properties, the crystal will grow spherically until a critical size is reached [29,33].

The condition \( \partial (\Delta G) / \partial (\Delta r) < 0 \) thus requires that \((r_P + \Delta r)G_v + 2\gamma_{SL} < 0 \)

Substituting \( \Delta G_v = -L_v \Delta T/T_m \) into Eq. (5) gives

\[
\Delta T > \frac{2\gamma_{SL}T_m}{L_v(r_P + \Delta r)}
\]

This defines the thermodynamic condition for \( \Delta G < 0 \). Considering that \( r_P + \Delta r > r_p \) and in most cases \( \Delta r \ll r_p \), it is easy to find that when the critical undercooling \((\Delta T_{crit})\) is set to be \((d_P = 2r_p)\)

\[
\Delta T_{crit} \approx \frac{4\gamma_{SL}T_m}{L_vd_P}
\]

Eq. (6) will always be satisfied. Eq. (7) defines an approximate critical undercooling for the nucleation of \( \Delta r \). It also defines the approximate condition for the formation of a grain as there is no barrier to subsequent growth. As evident from Eq. (7), \( \Delta T_{crit} \) decreases with increasing \( d_p \). The favourable substrate size is when \( d_P \to \infty \) at which \( \Delta T_{crit} \to 0 \), which means nearly barrierless nucleation. However, for nucleation on a given particle size, a critical undercooling is still required even if \( \theta = 0 \). This differs from
Fletcher’s model (spherical-cap) by which \( f(m, x) = 0 \) when \( \theta = 0 \) and accordingly no energy barrier to nucleation should exist.

It is interesting to note that Eq. (7) is of the same form as Eq. (1). On the one hand, this suggests that Turnbull’s patch nucleation criterion \( (d_p \geq 2\sigma^2) \) also approximately applies to nucleation on potent spherical substrates. Indeed, Eq. (7) is directly obtainable from the condition \( d_p \approx 2\sigma^2 \).

However, it should be pointed out that for nucleation on less potent spherical substrates \( (\theta > 20^\circ) \), Fletcher’s model \( (\text{spherical-cap}) \) by which the formation of a nucleus always means the formation of a grain. In contrast, Eq. (7) is derived on the basis of the barrier to growth after nucleation, which hinders a spherical-cap nucleus from growing into a transformation nucleus on a flat substrate. As such, the formation of a nucleus on a flat substrate does not necessarily mean the formation of a grain. In contrast, Eq. (7) is derived on the basis of the barrier to nucleation on a potent spherical substrate, where no barrier exists to subsequent growth. As a result, the formation of a nucleus always means the formation of a grain. Owing to the different geometries assumed for both the substrate and the nucleus, and the different mechanisms assumed for nucleation as well, Eqs. (1) and (7) can be regarded as two complementary models for nucleation and grain formation during solidification.

4. Comparison with experiments

4.1. Predicted dependency of \( \Delta T_{\text{crit}} \) on \( d_p \) and experimental observations

The thermochemical properties of magnesium have been well established. Substituting \( \gamma_{\text{sl}} = 115 \times 10^{-3} \text{J/m}^2 \) [34], \( L_v = 5.898 \times 10^8 \text{J/m}^3 \) [29] and \( T_m = 922 \text{K} \) into Eq. (7) gives

\[
\Delta T_{\text{crit}} = \frac{0.719}{d_p (\mu\text{m})}
\]

(8)

Fig. 4 plots the predicted dependency of \( \Delta T_{\text{crit}} \) on \( d_p \) over the size range 0.1–10 \( \mu\text{m} \) (most commonly used in practice) for inoculation of magnesium. Similar to the predictions made for inoculation of aluminium [6], effective inoculation of magnesium with potent spherical substrates depends on both the particle size and the undercooling of the melt experienced during solidification.

The predicted dependency in Fig. 4 provides a simple means of assessing the model at first glance. However, a number of difficulties exist for a rigorous comparison with experiment due to uncertainties concerning the measurement of \( \Delta T_{\text{crit}} \) and \( d_p \). First, when \( d_p > 1 \mu\text{m} \), \( \Delta T_{\text{crit}} \) is just a fraction of one degree Kelvin (Fig. 4). However, the experimental error \( (\Delta T_{\text{error}}) \) could reach \( \pm 0.4 \text{K} \) [35]. Second, the substrate particles contained in a master alloy are normally distributed in a wide range of size. For example, if nucleation first occurs on \text{Zr} \) particles of \( d_p > 2 \mu\text{m} \) (Fig. 2c), then the measured size is always smaller than the actual diameter of the nucleant unless one of its largest sections happens to be cut through.

Concerning the measurement of \( \Delta T \), in general, when there is obvious recalescence shown on the cooling curves, it can approximately be determined using an extrapolation approach, as shown by Johnson et al. [35]. However, when the recalescence is too small to be captured, it appears that \( \Delta T \) can only be approximately determined, directly from the cooling curve \( (T-t) \), in conjunction with the cooling rate curve \( (dT/dt-t) \). The underlying assumption is that \( \Delta T_{\text{error}} \) is consistent so that it will not affect the measurement of \( \Delta T \). That is, \( \Delta T = (T_n + \Delta T_{\text{error}}) - (T_{\text{eq}} + \Delta T_{\text{error}}) = T_n - T_{\text{eq}} \), where \( T_n \) is the temperature at which nucleation occurs. This is the approach adopted below.

A melt of 600 g pure magnesium was prepared in a mild steel crucible (dimensions: \( \phi = 68.6 \text{mm}; \; h = 155 \text{mm} \)) under the protection of \( 0.5\% \text{SF}_6 \) in dry air. The melt was inoculated with \( 1\% \text{Zr} \) at 730 °C using a Mg–33.3Zr master alloy (Fig. 2c). Samples were taken from the top of the melt using a conical steel ladle (dimensions: \( \varnothing 30 \text{mm} \times \varnothing 20 \text{mm} \times 25 \text{mm} \)), after 2 min of stirring following addition of the master alloy. The melt in the ladle was subsequently allowed to solidify in the air. A type K new thermocouple (0.5 mm diameter wire) was placed in the middle of the melt to record the thermal data through a data-logging system at an interval of 0.2 s.

Fig. 5a shows the cooling curve \( (T-t) \) obtained from analysing one such sample melt, and Fig. 5b is the cooling rate curve \( (dT/dt-t) \) corresponding to the period when nucleation occurs. The first obvious change in the cooling
The group of Zr particles of \( d_p < 1.0 \mu m \) shown in Fig. 6b, which account for about 10% of the active Zr nucleants observed, are not taken into account. This is because many of them appear to be just a portion of an actually larger particle when the etched surface was further slightly polished and examined. This points to the suggestion that all active Zr particles under the experimental conditions are most likely to be greater than 1 \( \mu m \). This is supported by the measured undercooling \( \Delta T_{n2} = 0.58 \) K, which gives a minimum Zr particle size of 1.24 \( \mu m \) by Eq. (8). Zr particles larger than 5 \( \mu m \) were observed, but few were found to be associated with a Zr-rich core, implying their ineffectiveness. As can be seen from Fig. 2(c), large Zr particles (\( d \geq 5 \mu m \)) have a very small particle density. Furthermore, not all of them may be effective. For example, in aluminium alloys, it has been found that only about 1–2% of the potential nucleant particles in an Al–Ti–B master alloy could contribute to grain refinement [2]. Another point to note is that large Zr particles are not still in molten magnesium due to their severe settling behaviour, as will be shown subsequently. These factors reduce the chance of large Zr particles acting as effective nucleants for magnesium grains.

### 4.2. Effect of settling and re-stirring on grain refinement

Owing to the marked difference in density (\( \rho_{Mg} = 1.58 \) g/cm\(^3\); \( \rho_{Zr} = 6.52 \) g/cm\(^3\)) and the low viscosity of molten magnesium, Zr particles settle fast in molten magnesium [37]:

\[
S \approx \frac{g(\rho_{Zr} - \rho_{Mg})d^2}{18\eta}t
\]

where \( S \) is the settling distance, \( g \) the gravitational acceleration, \( d \) the particle size and \( t \) the settling time. The density (\( \rho_{Mg} \)) and viscosity (\( \eta \)) of molten magnesium are functions of the melt temperature by \( \rho_{Mg} = 1.584 - 2.34 \times 10^{-4} (T - 650) \) [26] and \( \eta = 1.25 \times 10^{-3} - 2.54 \times 10^{-6} (T - 650) \) (N s m\(^{-2}\)), where the expression for \( \eta \) was extracted from the data of Fig. 1.9 in Ref. [38].

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Fig. 5. (a) Cooling curve (\( T-t \)) of a pure magnesium melt inoculated with 1%Zr and solidified at a cooling rate of 0.6 °C/s and (b) the cooling rate curve (\( dT/dt-t \)) corresponding to the period when nucleation occurs.
By settling, large Zr particles can be effectively removed from molten magnesium. According to the observations and predictions made earlier, Zr particles smaller than 1 μm are principally ineffective as nucleants for magnesium at the cooling rate of 0.6 °C/s. It follows that if all Zr particles larger than 1 μm are removed from a magnesium melt by settling, further settling, i.e. removal of smaller Zr particles, should have little effect on the inoculation process. This prediction will be tested below, again by comparing with an experiment reported previously but not understood properly [39].

The same experimental procedure described earlier was followed. After melting at 780 °C, the melt was inoculated with 1%Zr and then held for 360 min at 780 °C under the protection of SF₆. Samples were gently taken from the top of the melt at different times using a conical ladle, and the melt in the ladle was subsequently allowed to solidify in the air. Fig. 7 shows the resulting average grain size in each sample as a function of settling time. The grain size was observed to increase with increasing settling time in the first 120 min before subsequently levelling off.

We now apply the model to these observations. Since all samples were taken from the top of the melt using a small conical ladle, the height of the ladle, 25 mm, can be regarded as the depth of the melt from which each sample is taken. Thus, for a given settling time, all particles that have settled over 25 mm downwards from the top of the melt will be missed out in the sample cast. Taking 25 mm as the settling distance, the maximum particle size ($d_{\text{max}}$) remaining in the top 25 mm depth of the melt as a function of settling time can be predicted using Eq. (9). This is shown in Fig. 8. The predictions reveal that $d_{\text{max}} \approx 1.08$ μm after 120 min of settling. In other words, Zr particles of $d > 1.08$ μm have all settled out of the top of the melt within 120 min. The subsequent settling is thus mainly for particles of $d < 1.08$ μm. This is in excellent agreement with the 1 μm diameter prediction made earlier and explains why the grain size levelled off after 120 min of settling.

Also shown in Fig. 7 is that when the melt was re-stirred after a long settling period, samples that were taken from the top of the melt exhibited fine grain sizes again. This is because re-stirring the melt brought back the settled
particles of $d > 1.08 \, \mu m$ from the sludge to the melt. As a result, these particles acted as effective nucleants during solidification. This provides further support to the model.

4.3. Controlled columnar to equiaxed transition

The columnar to equiaxed transition (CET) can be induced by a number of mechanisms. However, when the melt contains potent substrates or a grain refiner, constitutional supercooling (CS)-driven heterogeneous nucleation is believed to play an important role [40]. Eq. (7) can be used as a basic tool to control the CET in the presence of a grain refiner.

Consider the solidification of a magnesium melt which has been subjected to sufficient settling after inoculation with Zr. The heat is conducted primarily away from the top of the melt. According to Eq. (7), if the undercooling created in the top of the melt is insufficient to activate the remaining Zr particles, few nucleation events should occur on these substrate particles. Consequently, columnar grains are expected to develop from the top along the direction of the heat flow. Once the CS ahead of the growing columnar front reaches the $\Delta T_{\text{crit}}$ required for nucleation on the remaining Zr particles by Eq. (7), the expected CET should occur. These predictions are tested below.

The experimental alloy used is Mg–3.8%Zn–2.2%Ca [28]. Its liquidus temperature is $\approx 632^\circ C$. A melt of 1250 g of the alloy was prepared at 730 °C and inoculated with 1.5% Zr. A conical mild steel mould was used to prepare the CET samples. The mould was thoroughly preheated at 730 °C. Then it was dipped into the melt and held for a further 15 min to ensure a uniform temperature. After that, the mould was withdrawn from the crucible and the melt in the mould was allowed to solidify in the closed furnace by switching off the power. The cooling rate recorded in the furnace averaged 1.2 °C/min. The mould was withdrawn from the furnace at 600 °C and cooled in the air afterwards.

Fig. 9 shows an overview of the CET observed in one of the conical samples prepared, and Fig. 10 is a detailed view showing the development of the columnar zone and the subsequent transition to equiaxed grains [28]. The CET occurred at about 3 mm below the melt surface. The observations shown in Figs. 9 and 10 are well reproducible. In addition, the depth of the columnar zone is controllable. These observations can be quantitatively understood using Eq. (7).

The melt in the conical mould was held for 15 min in the large crucible before cooling started. Together with the cooling time (0.02 °C/s) from 730 °C to the liquidus temperature 632 °C, the total settling time is 97 min. Substituting $t = 97$ min into Eq. (8) and taking $\rho_{\text{Mg}} = 1.584$ g/cm$^3$ and $\eta = 1.25 \times 10^{-3}$ N s/m$^2$ as specified previously gives

\[ S \approx 1.25 \times 10^4 d^2 \, (\mu m) \]  

(10)

Table 1 lists the maximum Zr particle sizes existing in different depths of the melt after 97 min of settling by Eq. (10), and the $\Delta T_{\text{crit}}$ required for nucleation on these particles by Eq. (8). As can be seen, for nucleation to occur on those Zr particles remaining in the very top surface layer (depth = 0.2 mm) of the melt, $\Delta T_{\text{crit}} = 5.71$ K is required. Given the very slow cooling rate (0.02 °C/s), it is difficult to generate such a level of thermal undercooling at the melt surface. Consequently, columnar grains rather than equiaxed grains are observed at the melt surface (Fig. 9).

Constitutional supercooling develops as the columnar grains grow into the melt. The very slow cooling rate adopted favours a flat temperature gradient ($G$) in the liquid ahead of the columnar front and therefore the development of CS. Assuming $G \approx 0$, the CS arising from the dissolved Zr in the liquid can be estimated as follows. The liquidus line on the Mg–Zr phase diagram [36] from pure magnesium to the peritectic composition (0.443% at 653.56 °C) is approximately given by

\[ T_l = 653.56 - \frac{3.56}{0.443} (0.443 - C_{Zr}) \]  

(11)

where $C_{Zr}$ is the Zr content. Fig. 11 summarises the Zr contents obtained from probing a total of 27 equiaxed grains just ahead of the columnar front in the sample shown in Fig. 10. The Zr contents detected are not uniform, but most measurements fall in the range 0.2–0.3%. The columnar grains at the interface were found to contain 0.0–0.15% Zr. So, away from the columnar front into the liquid there is a composition gradient of zirconium, and the variation is about 0.15% Zr over a few grains of distance.
Such a gradient can give rise to a difference of 1.21 K in the melting point by Eq. (11), which is equivalent to 1.21 K of CS when \( G \). This is fairly close to the \( D_{\text{crit}} \) (1.46 K, Table 1) required for nucleation on the Zr particles (\( d_{\text{max}} = 0.49 \mu m, \) Table 1) remaining in the top 3 mm depth of the melt. If the CS arising from the contributions of Zn and Ca were taken into account, it would be reasonable to suppose that the actual CS created ahead of the 3 mm deep columnar zone is around 1.46 K. The theory thus predicts and explains the observations well.

In a recent development [29], it has been shown that spherical primary magnesium crystals are obtainable directly from the liquid state, without liquid agitation, through effective control of nucleation and growth by grain refinement with Zr. Eq. (1) was used to quantitatively understand the nucleation on nearly spherical zirconium particles because of the lack of a more suitable model at that time. Apparently, Eq. (7) will give exactly the same predictions but on a more reasonable fundamental basis. This can be regarded as another example of microstructural control on the basis of Eq. (7).

### Table 1

<table>
<thead>
<tr>
<th>Depth of melt (mm)</th>
<th>Maximum Zr particle size remaining in depth (µm)</th>
<th>( D_{\text{crit}} ) required for nucleation on remaining Zr particles (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.126</td>
<td>5.71</td>
</tr>
<tr>
<td>1</td>
<td>0.28</td>
<td>2.54</td>
</tr>
<tr>
<td>2</td>
<td>0.40</td>
<td>1.80</td>
</tr>
<tr>
<td>3</td>
<td>0.49</td>
<td>1.46</td>
</tr>
<tr>
<td>4</td>
<td>0.57</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Such a gradient can give rise to a difference of 1.21 K in the melting point by Eq. (11), which is equivalent to 1.21 K of CS when \( G \approx 0 \). This is fairly close to the \( D_{\text{crit}} \) (1.46 K, Table 1) required for nucleation on the Zr particles (\( d_{\text{max}} = 0.49 \mu m, \) Table 1) remaining in the top 3 mm depth of the melt. If the CS arising from the contributions of Zn and Ca were taken into account, it would be reasonable to suppose that the actual CS created ahead of the 3 mm deep columnar zone is around 1.46 K. The theory thus predicts and explains the observations well.

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### 5. Summary

- A model has been proposed for heterogeneous nucleation and grain formation on potent spherical particles during solidification on the basis of an adsorption and surface diffusion mechanism, where nucleation is assumed to occur through the formation of an adsorbed layer of atoms that is characteristic of the structure of the crystal. The critical undercooling required for such a nucleation event is proportional to the reciprocal of the substrate size and is defined approximately by \( \Delta T_{\text{crit}} = \frac{4\gamma_{\text{Sl}} T_m}{L_v d_p} \).
The excellent agreement achieved with experiments, compared from different perspectives, indicates that the proposed model can describe the experiments well. It thus provides a useful tool for microstructural control via effective inoculation with spherical substrates, as has been demonstrated on magnesium alloys.

Owing to the different geometries assumed for both the substrate and the nucleus, and the different mechanisms assumed for nucleation as well, Turnbull’s patch nucleation theory, or the free growth model, and the present model can be regarded as complementary models for nucleation and grain formation during solidification. However, for nucleation on less potent spherical substrates ($\theta > 20^\circ$), Fletcher’s model still gives the most reasonable description.

Effective inoculation with potent spherical substrates depends on both the substrate sizes and the undercooling that the liquid metal experiences during solidification. For a given size of potent spherical substrate, a critical undercooling is still required for nucleation even if the contact angle is zero. Barrierless nucleation appears to be possible only when the particle size approaches infinity under complete wetting conditions.

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References

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