Mechanisms of grain refinement by intensive shearing of AZ91 alloy melt

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Abstract

It has been demonstrated recently that intensive melt shearing can be an effective approach to the grain refinement of both shape casting and continuous casting of Mg alloys. In the present study, the mechanisms of grain refinement by intensive melt shearing were investigated through a combination of both modelling and experimental approaches. The measurement of the cooling curves during solidification, quantification of grain size of the solidified samples, and image analysis of the MgO particle size and size distribution in the pressurized filtration samples were performed for the AZ91 alloy with and without intensive melt shearing. The experimental results were then used as input parameters for the free growth model to investigate the mechanisms of grain refinement by intensive melt shearing. The experimental results showed that, although intensive melt shearing does not change the nucleation starting temperature, it increases the nucleation finishing temperature, giving rise to a reduced nucleation undercooling. The theoretical modelling using the free growth model revealed quantitatively that intensive melt shearing can effectively disperse MgO particles densely populated in the oxide films into more individual particles in the alloy melt, resulting in an increase in the MgO particle density by three orders of magnitude and the density of active nucleating MgO particles by a factor of 20 compared with those of the non-sheared melt. Therefore, the grain refining effect of intensive melt shearing can be confidently attributed to the significantly increased refining efficiency of the naturally occurring MgO particles in the alloy melt as potent nucleation sites.

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1. Introduction

A fine and fully equiaxed microstructure is desirable for both cast and wrought alloys, since it improves the casting processes, facilitates downstream processing and enhances the mechanical properties of the as-cast components [1,2]. Grain refinement can usually be achieved through enhancing heterogeneous nucleation during solidification processing by either chemical inoculation [2,3] or physical grain refinement [4]. Chemical inoculation is achieved by the addition of a specially selected chemical substance (the grain refiner) to provide exogenous crystalline particles to the alloy melt prior to solidification processing, e.g., TiB₂ and TiC for Al-alloys and Zr for Al-free Mg alloys. In contrast, physical grain refinement relies on activating the endogenous crystalline particles naturally occurring in the alloy melt by physical means such as magnetic stirring, ultrasonic streaming and intensive melt shearing. It has been demonstrated in recent years that intensive melt shearing provided by the MCAST process can be an effective approach for physical grain refinement [4]. The MCAST process has been developed to condition alloy melts prior to solidification processing, and solidification of the intensively sheared alloy melt results in significant grain refinement, considerable reduction of cast defects and substantial improvement in the mechanical properties.
of the solidified materials [4–8]. For example, the grain size was reduced from 682 μm without intensive melt shearing to 178 μm with intensive melt shearing in the typical TP-1 test samples for the AZ91 alloy at a casting temperature of 650 °C [4]. This process is particularly useful for grain refinement of the Al-bearing Mg alloys, for which, zirconium, as the efficient grain refiner for the Al-free Mg alloys, is poisoned [9], and effective grain refiners for such alloys remain an active research topic [10–16]. Thus, elucidating the mechanisms of the grain refinement by intensive melt shearing is of significant importance for both scientific understanding and technological development.

For effective grain refinement, the nucleating particles need to be highly potent, i.e., with a very small nucleation barrier [2–4]. This is only possible while a lattice plane of the nucleating substrate exhibits a good atomic match with a lattice plane of the nucleated solid, and the atomic mismatch is typically <10% for potent particles [17]. In a previous study [4], a well-defined orientation relationship was observed between the MgO and α-Mg phases: (1210)$_{\text{Mg}}$/⟨011⟩$_{\text{MgO}}$ and {0 0 0 2}$_{\text{Mg}}$/⟨1 1 1⟩$_{\text{MgO}}$. It was found that the crystallographic misfit along the most closely packed directions ((1210)$_{\text{Mg}}$/⟨011⟩$_{\text{MgO}}$) on the most closely packed atomic planes is only 5.46%. With such potent nucleation particles, the classical spherical-cap model for heterogeneous nucleation may not be applicable [18]. The adsorption model [18,19] and hypernucleation theory [20,21] may be more appropriate for such cases.

Quantitative prediction of nucleation events during solidification of metallic liquids is not a trivial task [22]. Maxwell and Hellawell [23] applied the classical steady-state nucleation theory to calculate the number of heterogeneous nucleation events in a spatially isothermal melt as a function of the density of the nucleating particles with a single particle size. The final grain size was taken as the result of a competition between heterogeneous nucleation and growth in the melt. The nucleation rate was believed to be negligible when the temperature rises due to latent heat evolved by the growth of the new phase (recalescence) or when the nucleation sites are exhausted. Based on the Maxwell–Hellawell model, Greer et al. [24] developed the free growth model for grain initiation on potent nucleating substrates. This model suggested that a new crystalline phase could start free growth, without any delay, on the potent particles at an undercooling inversely proportional to the diameter of the nucleating substrate. Unlike the Maxwell–Hellawell model, the grain initiation in the free growth model is neither time dependent nor stochastic, and a distribution of particle sizes was applied rather than a single size. The free growth model revealed that the largest particles in the melt start to grow first, as soon as the required undercooling is reached, followed by the progressively smaller ones as the undercooling is increased. Grain sizes are limited by recalescence, after which no further grain initiation occurs. With size distribution of the particles as input parameters, the free growth model has been successfully applied in the cases of aluminium alloys inoculated by the Al-Ti-B and Al–Ti-C based grain refiners [24,25] and magnesium alloy by the SiC refiner [26].

The objective of the present study was to elucidate the mechanisms of grain refinement by intensive melt shearing through the combination of theoretical modelling based on the free growth model and experimental investigation. The free growth model was applied to study quantitatively the initial stage of solidification in the sheared and non-sheared AZ91 alloy melt. The modelling results, combined with the experimental observations, are used to understand the roles of the MgO particles in grain initiation during solidification with and without prior intensive melt shearing.

2. Experimental and modelling procedures

2.1. Cooling curves during solidification and the resultant microstructures

Fig. 1 shows a schematic illustration of the experimental set-up for measuring the cooling curves during solidification of the AZ91 alloy melt. The inner steel crucible, covered with a 13-mm-thick layer of thermal insulation, was placed in the centre of an outer crucible to ensure consistent cooling conditions by minimizing the influence of the environment. The AZ91 alloy ingot (Mg–8.6Al–0.67Zn–0.22Mn, all in wt.%) was melted at 680 °C under a protective gas mixture (N$_2$ containing 0.4 vol.% SF$_6$). The alloy melt was then transferred to the MCAST unit and sub-

![Fig. 1. Schematic illustration of the experimental set-up for measuring the cooling curves of the AZ91 alloy melt with and without prior intensive melt shearing. The inner steel crucible, covered by a 13-mm-thick thermal insulation, was placed in the centre of a larger outer crucible to ensure consistent cooling conditions. The alloy melt with or without prior intensive melt shearing was poured into the inner crucible, and covered immediately by a thin layer of salt flux and a steel lid to prevent oxidation. A K-type thermocouple with diameter 0.5 mm supported by a steel tube was located in the centre of the inner crucible to measure the melt temperature, and temperature data were recorded at a frequency of 20 Hz.](image-url)
ject to intensive shearing at 800 rpm for 45 s at 650 °C. The alloy melt with or without melt shearing was poured into the inner crucible pre-heated to 650 °C, and was immediately covered by a thin layer of salt flux and a steel lid to protect the melt from oxidation. A Ø0.5 mm K-type thermocouple supported by a Ø3 mm steel tube fixed on the lid was located in the centre of the inner crucible to measure the melt temperature. The melt temperature was recorded through a data logger with a frequency of 20 Hz.

Samples for microstructural analysis were taken from the central position (the position of the thermocouple tip) of the solidified ingot. The microstructures were quantified to obtain the grain sizes of both sheared and non-sheared samples. Metallographic sections for optical microscopy (OM) were prepared using standard metallographic procedures, followed by colour etching [27]. The grain size is the value of mean linear intercept length \(l\). The number of grains per unit volume \(N_s\) is obtained using the following equation [24]:

\[
N_s = \frac{0.5}{l}
\]

(1)

where \(N_s\) is taken as the lower bound of the number density of the active nucleating particles in the melt, and is used as the number density of active nucleating particles \(N_e\).

2.2. Measuring the MgO particle size distribution

The size distribution of MgO particles in the sheared melt was obtained by analysing the pressurized filtration samples with intensive melt shearing. The oxide and intermetallic inclusions in the sheared AZ91 melt were collected by the pressurized filtration technique, as described in detail elsewhere [4]. The solidified material adjacent to the filter with a high concentration of inclusion particles was sectioned and prepared for detailed metallographic examination. Metallographic sections for scanning electron microscopy (SEM) were prepared using standard metallographic procedure. The SEM examination was carried out using a Zeiss Supera 35 FEG microscope, equipped with an energy dispersive spectroscopy (EDS) facility, operated at an accelerating voltage of 5–15 kV. Image analysis was used to obtain the size distribution of MgO particles from the SEM micrographs.

2.3. Modelling method

The particle size distribution is a crucial factor in nucleation analysis. Turnbull [28] derived the size distribution of nucleating patches by fitting the data on solidified fraction of the undercooled liquid mercury droplets. Greer et al. [24] reversed this procedure by using the size distribution of nucleating particles (TiB\(_2\)) determined experimentally from the grain refiner alloy (Al–5Ti–1B, all in wt.%) to predict quantitatively the grain size of the inoculated aluminium alloys. The population distribution of the TiB\(_2\) particles was found to follow a log-normal function [25]:

\[
N(d) = \frac{N_0}{\sigma d \sqrt{2\pi}} \exp\left(-\frac{(\ln(d) - \ln(d_0))^2}{2\sigma^2}\right)
\]

(2)

where \(d_0\) is the geometric mean diameter, \(\sigma\) is the geometric standard deviation, \(N(d)\) is the number of particles of diameter between \(d\) and \(d + \Delta d\), and \(N_0\) is the total number of particles. The required undercooling for free growth on a given particle \(\Delta T_{tg}\) is simply related to its diameter \(d\) by [24]

\[
\Delta T_{tg} = \frac{4\gamma}{\Delta S_v d}
\]

(3)

where \(\gamma\) is the solid–liquid interfacial energy, and \(\Delta S_v\) is the entropy of fusion per unit volume.

However, the approach adopted by Greer et al. to obtain particle size distribution cannot be applied in the case of physical grain refinement. Here, a different approach to obtaining the size distribution of MgO particles in the intensively sheared alloy melt is proposed. For convenience, the grain initiation will be referred to as nucleation from now on. First, the maximum undercoolings of the sheared and non-sheared AZ91 alloy melt are obtained from the measured cooling curves. In the present study, the temperature at which the cooling curve starts to deviate from linearity is defined as the nucleation starting temperature \(T_n\), and the minimum temperature before recalescence as the nucleation finishing temperature \(T_f\). The temperature interval between the alloy liquidus \((T_l)\) and \(T_f\) is taken as the maximum undercooling for nucleation, \(\Delta T_{max}\), i.e., the undercooling required for the smallest particles which have participated in the nucleation process. In addition, the diameter of the smallest active particles is defined as the critical diameter \(d_c\). According to Eq. (3), \(d_c\) can be determined from \(\Delta T_{max}\). Second, the number density of the active nucleating particles is estimated from the grain size of the corresponding solidified samples according to Eq. (1). Thirdly, the size distribution \((\sigma\) and \(d_0\)) of MgO particles in the sheared melt is obtained from the image analysis of the MgO particles in the pressurized filtration samples. The integration of \(N(d)\) from \(d_c\) to the maximum particle size \(d_{max}\) provides the number density of active nucleating particles \(N_e\). The minimum particle size used in this modelling is denoted as \(d_{min}\). Therefore, the total number of MgO particles \(N_0\) and then the population density \(N(d)\) (from \(d_{min}\) to \(d_{max}\)) can be obtained by applying Eq. (2) with \(N_e\), \(d_c\), \(\sigma\) and \(d_0\) as input parameters.

After the particle size distribution had been obtained, the treatment used by Greer et al. [24,25] for grain initiation was followed closely. However, a dendritic growth model instead of a spherical growth model was applied in the present modelling. Dendrites can grow with a tip undercooling \(\Delta T\), which depends on growth velocity \(V\), temperature gradient \(G\) and alloy composition \(C_0\) [29]. Empirically, it was found [30,31] that

\[
\Delta T = \frac{GD}{V} + \left(\frac{C_0V}{A}\right)^{1/2}
\]

(4)
with

\[ A = \frac{D}{8m(1 - k)\Gamma} \]  

where \( D \) is the self-diffusion coefficient in liquid, \( m \) is the liquidus slope, \( k_0 \) is the distribution coefficient, and \( \Gamma \) is the Gibbs–Thomson parameter

\[ \Gamma = \frac{\gamma}{\Delta S_v} \]  

Under the assumption of an isothermal melt, the growth velocity of the dendrite tip can be given as

\[ V = \frac{A\Delta T^2}{C_0} \]  

The numerical calculation was implemented in Visual Basic 6.0, and the undercooling increment between steps was typically 0.01 K. All the relevant parameters and their typical values used in the modelling are listed in Table 1.

3. Results

3.1. Measured cooling curve and grain size

Fig. 2 shows the experimentally determined cooling curves for the AZ91 alloy melt with and without intensive melt shearing. Near the liquidus \( (T_l) \), the typical cooling rate is \(-0.22 \degree C \text{s}^{-1}\) in the sheared melt, and \(-0.2 \degree C \text{s}^{-1}\) in the non-sheared melt. Both cooling curves show pronounced recalescence, agreeing with the basic feature of the free growth model [24]. Because it is not possible to obtain an accurate value of \( T_l \) from the measured cooling curve, the experimental \( \Delta T_{\text{max}} \) is approximately determined relative to the thermal plateau temperature after recalescence \( T_r \). Usually the value of \( T_l - T_r \) is small, corresponding to the required undercooling for crystal growth during solidification. Therefore, the value of \( T_r - T_l \) is used as a good approximation of \( \Delta T_{\text{max}} \), which is marked in Figs. 2 and 3. The measured \( \Delta T_{\text{max}} \) is 0.62 \degree C with intensive melt shearing and 0.98 \degree C without intensive melt shearing. From Eq. (3), \( d_s \) was then determined as 0.95 \text{mum} with intensive melt shearing and 0.60 \text{mum} without intensive melt shearing.

Fig. 3 shows a schematic illustration of a typical cooling curve, the first derivative \((\partial T/\partial t)\) and the second derivative \((\partial^2 T/\partial t^2)\) of the cooling curve following the treatment used in Refs. [33, 34]. It is almost impossible to determine \( T_s \) from the original cooling curve, but \( T_s, T_f \) and \( T_r \) can be easily identified in the first and second derivatives of the cooling curves. The average values and the corresponding standard deviations of the measured \( T_s, T_f \) and \( T_r \) from nine original cooling curves (five for non-sheared melt and four for sheared melt) are presented in Table 2. First, the values for \( T_r \) are almost identical for the non-sheared and sheared melts, indicating that the size of the largest particle that triggers nucleation is the same for both the sheared and non-sheared melts; secondly, the value of \( T_l \) in the sheared melt is 0.4 \degree C higher than that in the non-sheared melt, suggesting that intensive melt shearing decreases the maximum nucleation undercooling \( (\Delta T_{\text{max}}) \) and gives a larger critical size for nucleation \( (d_s) \); thirdly, \( T_f \) is not changed by intensive melt shearing, implying that intensive melt shearing does not change the growth temperature. This confirms for the first time that intensive melt shearing only disperses particle agglomerates into individual particles, without breaking up the larger particles into smaller ones. This means that intensive melt shearing only promotes a uniform spatial distribution of the MgO particles in the entire volume of the alloy melt without changing the particle size and size distribution.

The average grain size of the solidified samples was determined as 2005 \text{mum} for the non-sheared samples and 1210 \text{mum} for the sheared samples. According to Eq. (1), the number density of active nucleating particles \( (N_c) \) is

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Units</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbs–Thomson parameter</td>
<td>( I )</td>
<td>Km</td>
<td>( 1.48 \times 10^{-7} )</td>
<td>[32]</td>
</tr>
<tr>
<td>Enthalpy of fusion per unit volume</td>
<td>( \Delta H_c )</td>
<td>J m(^{-3})</td>
<td>( 6.75 \times 10^8 )</td>
<td>[32]</td>
</tr>
<tr>
<td>Heat capacity of melt per unit volume</td>
<td>( C_v )</td>
<td>J K m(^{-3})</td>
<td>( 2.59 \times 10^6 )</td>
<td>[32]</td>
</tr>
<tr>
<td>Diffusivity in melt (Al in Mg)</td>
<td>( D )</td>
<td>m(^2) s(^{-1})</td>
<td>( 2.7 \times 10^{-9} )</td>
<td>[32]</td>
</tr>
<tr>
<td>Liquidus slope</td>
<td>( m )</td>
<td>Kg wt.%</td>
<td>(-6.87)</td>
<td>[3]</td>
</tr>
<tr>
<td>Equilibrium partition coefficient</td>
<td>( k )</td>
<td></td>
<td>0.37</td>
<td>[3]</td>
</tr>
</tbody>
</table>
be well fitted by Eq. (2), and the curve in the figure is indicative of the fitted log-normal function with $d_0 = 0.07 \, \mu m$ and $\sigma = 0.45$.

### 3.3. Population distribution of MgO particles

The total number of MgO particles ($N_0$) can be calculated from Eq. (2) with $\sigma$, $d_0$, $N_c$ and $d$ as input parameters. $N_0$ was determined as $3.2 \times 10^8 \, mm^{-3}$ and $2.1 \times 10^5 \, mm^{-3}$ for the sheared and non-sheared alloy melt, respectively. It is interesting to note that the value of $N_0$ for the non-sheared melt is very close to the total number ($5 \times 10^6 \, mm^{-3}$) of TiB$_2$ particles with the addition of 1 ppt Al-5Ti-1B grain refiner [24]. This indicates that as far as heterogeneous nucleation is concerned, there are sufficient numbers of naturally occurring MgO particles in the alloy melt prepared under standard melting conditions. The purpose of physical grain refining is to increase the efficiency of such endogenous particles for enhanced heterogeneous nucleation.

The MgO population density ($N(d)$) can then be obtained from Eq. (2) using $d_{\text{min}}$, $d_{\text{max}}$, $\sigma$, $d_0$ and $N_0$ as input parameters. Fig. 6a shows the calculated $N(d)$ for the MgO particles as a function of $d$ in the sheared melt using $\sigma = 0.45$, $d_0 = 0.07 \, \mu m$, $d_{\text{min}} = 0.01 \, \mu m$ and $d_{\text{max}} = 6.0 \, \mu m$. Repeated calculations using different sets of $d_{\text{min}}$ and $d_{\text{max}}$ have shown that the range of particle sizes used for the calculations has little effect on the resultant population density. Since intensive melt shearing only disperses MgO particles agglomerates into individual particles without changing the actual size of individual particles, as discussed in Section 3.1, the size distribution ($\sigma$ and $d_0$) of MgO particles in the non-sheared melt is assumed to be the same as that in the sheared melt. Fig. 6b shows the calculated $N(d)$ as a function of $d$ for the non-sheared melt. Comparing Fig. 6a with Fig. 6b, it can be concluded that the density of the potential nucleating sites in the sheared melt is about three orders of magnitude higher than that in the non-sheared melt, clearly showing the power of intensive melt shearing.

### 3.4. Validation of the free growth model

Once all the necessary parameters are in place, it is possible to apply the free growth model to predict the solidification process and the resultant microstructures under different solidification conditions, and then to compare the model predictions with the experimental results as a direct validation of the free growth model. Fig. 7 shows the simulated cooling curves with and without intensive melt shearing. The cooling rate used in the simulation is

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**Table 2**

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_s$ (°C)</th>
<th>$T_f$ (°C)</th>
<th>$T_r$ (°C)</th>
<th>$\Delta T_{\text{max}}$ (°C)</th>
<th>Grain sizes (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without shearing</td>
<td>597.97 ± 0.07</td>
<td>597.05 ± 0.12</td>
<td>598.15 ± 0.12</td>
<td>0.98 ± 0.14</td>
<td>2005</td>
</tr>
<tr>
<td>With shearing</td>
<td>597.91 ± 0.12</td>
<td>597.47 ± 0.10</td>
<td>598.15 ± 0.12</td>
<td>0.62 ± 0.07</td>
<td>1210</td>
</tr>
</tbody>
</table>
0.22 °C s⁻¹ with intensive melt shearing, and 0.2 °C s⁻¹ without intensive melt shearing, which are the same as the experimental conditions. The calculated ΔTₘₐₓ is 0.71 °C with intensive melt shearing, and 0.99 °C without intensive melt shearing. The grain size predicted by the model is 0.671 mm with intensive melt shearing and

1.931 mm without intensive melt shearing. The theoretical predictions (Fig. 7) are in good agreement with the experimental results (Fig. 2) both in sheared and non-sheared cases.
Fig. 8 shows the theoretically predicted nucleation finishing temperatures ($T_f$) and the solid fraction at $T_f$ as a function of cooling rate. Fig. 8a reveals that $T_f$ decreases with increase in cooling rate, although the predicted $T_f$ for the sheared melt is always higher than that for the non-sheared melt at the same cooling rate, which is consistent with experimental observations (Fig. 2). Fig. 8b shows that the solid fraction at $T_f$ increases with increase in cooling rate, and that at a cooling rate of 0.2 °C/s, the predicted solid fraction at $T_f$ for the non-sheared melt is 0.024%, which is greater than 0.015% predicted for the sheared melt. It is interesting to note that the predicted solid fraction at $T_f$ has the same order of magnitude as that obtained by Quested and Greer in the inoculated Al melt (~0.02%) [25]. At $T_f$, the latent heat released from the growing solid phase is balanced by the heat extraction from the solidification environment, and further growth of the solid phase will cause recalescence. Therefore, increasing the cooling rate reduces the nucleation finishing temperature $T_f$, which will, in turn, increase the solid fraction at $T_f$.

The good agreement between the theoretical predictions and the experimental observations suggests that the free growth model can be applied reliably in both sheared and non-sheared cases to investigate the grain refining mechanisms of AZ91 alloy with intensive melt shearing.

3.5. Mechanisms of grain refinement by intensive melt shearing

Fig. 9a shows the theoretically predicted number density of active nucleating particles as a function of cooling rate. Although the number of active particles increases with the increase in cooling rate in both the sheared and non-sheared cases, the increase in the sheared melt is much more pronounced than that in the non-sheared melt. For instance, at a cooling rate of 0.2 °C/s, the number density of active particles is 1.5 mm$^{-3}$ and 0.07 mm$^{-3}$ for the cases with and without intensive melt shearing, respectively. This means that the number density of active particles is increased by a factor of 20 by the intensive melt shearing. Table 3 summarizes the physical parameters extracted by the theoretical analysis.

The dramatic increase in the number density of active nucleating particles can be attributed to the dispersive function of intensive melt shearing. In the non-sheared melt, the nucleation of the $\alpha$-Mg phase first occurs on the largest MgO particle available in the oxide film, and the smaller particles in the same oxide film are made redundant owing to the local temperature rise caused by the release of...
latent heat, resulting in the complete engulfment of the rest of the particles in the growing solid phase. The number of active particles in the non-sheared melt is therefore determined by the number of the oxide films, which can only act as single entities for heterogeneous nucleation. This argument is supported by the fact that the resultant average grain size (2 mm) is much larger than the size of the largest oxide film (about a few hundred microns) [4]. With intensive melt shearing, the MgO particles in the oxide films were effectively dispersed into a greater number of individual particles, resulting in an increase of three orders of magnitude in the total number of MgO particles in the sheared melt as presented previously. According to Eq. (2), the number of active particles in the sheared melt would be expected to be in the same order of magnitude at the same $\Delta T_{\text{max}}$. However, $T_i$ in the sheared melt is higher than that in the non-sheared melt at the same cooling rate (Fig. 8a), and hence $\Delta T_{\text{max}}$ of the sheared melt is smaller than that of the non-sheared melt. As a consequence, the effective increase in active particles in the sheared melt is only by a factor of 20, compared with that in the non-sheared melt. This substantial increase in the number of active nucleating particles by intensive melt shearing will naturally lead to a significant reduction in grain size, as shown in Fig. 9b. At a cooling rate of 0.2 °C s$^{-1}$, the predicted grain size is reduced from 1.931 mm for the non-sheared melt to 0.691 mm for the sheared melt. Furthermore, Fig. 9b shows that the grain refining effect by intensive melt shearing is more pronounced at low cooling rates than that at high cooling rates.

### 4. Discussion

Owing to the assumption of an isothermal melt, the free growth model is usually applicable for a small volume of melt solidifying under a low cooling rate, such as in the case of the standard TP-1 test with a cooling rate of $\sim$3.5 K s$^{-1}$ and a melt volume of $\sim$100 cm$^3$ [35]. In the present experiments, the maximum volume of the melt is 157 cm$^3$, and the measured cooling rate is $\sim$0.22 °C s$^{-1}$ at temperatures close to the alloy liquids. Such solidification conditions can be regarded, to a reasonably good approximation, as being isothermal. This justifies the application of the free growth model for the simulation of the solidification process under the current experimental conditions.

The free growth model requires that the particles are potent for heterogeneous nucleation. Generally, the $\Delta T_{\text{max}}$ is small for potent nucleating particles, and increases with the reduction in the average size of the active nucleating particles according to Eq. (3). Eq. (3) holds true at temperatures near $T_i$, and may become less valid with increasing $\Delta T$ [36,37]. Thus, the relatively small particles used in this modelling may lead to some degree of uncertainty in the simulation results. In addition, the cooling rate, as an input parameter, has a significant effect on the simulation results, as shown in Figs. 8a and 9b. The cooling rates used in the modelling according to the measured cooling curves may also lead to a minor discrepancy between the experimental and simulation results. All these factors contribute to the discrepancy between the simulation results and the experimental observations. However, the theoretically predicted cooling curve and grain size of the solidified samples exhibit good agreement with the experimental results for both the non-sheared and sheared melts, supporting the validity of using the current modelling on the free growth model. Therefore, the free growth model can be applied with great confidence to study quantitatively the solidification process in the intensively sheared melt under quasi-isothermal conditions.

Grain refinement by intensive melt shearing derives primarily from the effective dispersion of the MgO particles in the naturally occurring oxide films into fine dispersion of individual particles in the melt. Since the MgO particles are loosely packed (although densely populated) inside the oxide films, dispersion of such oxide particles can be achieved relatively easily if the shear rate and the shearing time are beyond a critical level [4]. Once all the MgO particles in the oxide films have been completely dispersed into individual particles, further increase in shearing will not achieve further grain refinement. In addition, the solubility of oxygen in the Mg alloy melt is very low, suggesting that neither could the largest particles grow nor could the smallest particles dissolve in the melt during intensive melt shearing. Therefore, both the size and size distribution of the MgO particles will remain unchanged during intensive melt shearing.

Intensive melt shearing led to an increase in the total number of MgO particles in the sheared melt by three orders of magnitude compared with that in the non-sheared melt. As a consequence, the density of active MgO particles in the sheared melt is increased by a factor of 20 under the same solidification conditions. Thus, the grain size with melt shearing becomes considerably finer than that without melt shearing. The efficiency of the nucleating particles can be defined as the ratio of the number of active nucleating particles to the total number of potential nucleating particles. As mentioned previously, the total

### Table 3

Physical parameters extracted by theoretical analysis at a cooling rate of 0.2 °C s$^{-1}$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$d_e$ (μm)</th>
<th>$d_o$ (μm)</th>
<th>$\sigma$</th>
<th>$N_e$ (mm$^{-3}$)</th>
<th>$N_f$ (mm$^{-3}$)</th>
<th>Solid fraction at $T_i$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without shearing</td>
<td>0.60</td>
<td>0.07</td>
<td>0.45</td>
<td>$2.1 \times 10^4$</td>
<td>0.07</td>
<td>0.024</td>
</tr>
<tr>
<td>With shearing</td>
<td>0.95</td>
<td>0.07</td>
<td>0.45</td>
<td>$3.2 \times 10^4$</td>
<td>1.5</td>
<td>0.015</td>
</tr>
</tbody>
</table>

number of MgO particles does not change during intensive melt shearing, while the number of active particles increases dramatically. Consequently, the efficiency of the MgO particles in the sheared melt is much higher than that in the non-sheared melt. The significant improvement in the efficiency of MgO particles leads to effective grain refining in the sheared melt.

5. Summary

This work investigated grain refining mechanisms by intensive melt shearing prior to solidification processing through coupling of the experimental and modelling approaches. The experimental approach was used to obtain cooling curves during solidification under quasi-isothermal conditions, the MgO particle size and size distribution in the alloy melt and the resultant grain size in the solidified samples. Experimental results were then used as input parameters for the free growth model to analyse quantitatively the nucleation behaviour of AZ91 alloy melt with and without melt shearing.

The experimental results showed that, although intensive melt shearing does not change the nucleation starting temperature, it does increase the nucleation finishing temperature and consequently decreases the maximum nucleation undercooling. The experimental results also revealed that the total number of MgO particles in the AZ91 alloy melt is $2.1 \times 10^5 \text{ mm}^{-3}$, which is comparable with that of TiB$_2$ particles with the addition of 1 ppt Al–5Ti–1B grain refiner ($5 \times 10^4 \text{ mm}^{-3}$), confirming that there are sufficient endogenous particles in the non-sheared alloy melt for potential heterogeneous nucleation sites. Intensive melt shearing can increase the MgO number density to $3.2 \times 10^8 \text{ mm}^{-3}$, which is about three orders of magnitude higher than that in the non-sheared melt. It was found that the density of the active MgO particles in the sheared melt is $\sim 20$ times higher than that in the non-sheared melt, giving rise to significant grain refinement.

The free growth model was successfully applied to study quantitatively the nucleation process in both the sheared and non-sheared AZ91 alloy melt, with the size distribution of MgO particles as an input parameter. The calculated cooling curves and grain sizes are in good agreement with the experimental results. The mechanisms of grain refinement in the intensively sheared AZ91 alloy melt were investigated according to the modelling results and experimental observations. It has been shown quantitatively that the MgO particles in the oxide films were effectively dispersed into more individual particles by intensive melt shearing. This significantly increased the number density of the active nucleant particles in the sheared melt and, consequently, achieved significant grain refinement.

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References