Solid-liquid interface dynamics during solidification of Al 7075-Al₂O_{3np} based metal matrix composites

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ABSTRACT

Interactions between the solidification front and the remaining suspended particles take place during solidification of particles reinforced composites. The particles are either engulfed by the solidification front or pushed by the solid-liquid interface. In this study, the relation of distribution and clustering degree of nano-Al₂O₃ in Al7075 with the microstructure of alloy was investigated by conducting casting experiment. A hydrodynamic model for calculating the critical interface velocity required to push nano-particles by the interface was proposed. In addition, the influence of the nano-particles present ahead of solidification front on interface shape was discussed. Microstructural studies showed that the resulting microstructures of composites depended on the size and degree of nano-Al₂O₃ clustering. Based on the model, it was found that for particles below approximately 36% of the critical radius, $r < 0.36r^* = 0.9973 \mu\text{m}$, the critical interface velocities were four orders of magnitude lower than those obtained by micron particles, suggesting that smaller particles are easily engulfed by the interface rather than pushed. The experimental results were validated by the prediction of the model. Result showed that the constitutional super-cooling of local melts and the accumulation of solute behind the particle caused formation of a cellular interface.

Keywords: Metal-matrix composites; Nano-particles; Critical interface velocity; Interface shape; Ultrasonic vibration.

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1. Introduction

Aluminum matrix composites reinforced with nano-particles are widely used in automotive, military and aerospace industries because of their improved mechanical properties, such as high-temperature creep resistance, greater durability under fatigue life and good wear resistance [1-4]. In the recent years, much of composites research has been focused on the dispersion and distribution of nano-particles in a matrix, which significantly affects microstructure and properties of the composites [2, 5-6]. It is of interest to note that the particles with different sizes are distributed at different regions of the matrix. The aggregates are located along grain boundaries and the large aggregates are distributed in the grain and last freezing interdendrite region, which suggests that the distribution of particles is related to the solidification behavior. When alloy melts containing suspended particles solidify, interactions between the solidification front and the remaining suspended particles take place, resulting in changed particle distribution. The particles are either engulfed by the solidification front, and thus distributed within the grain, or pushed by the solid-liquid interface toward the grain boundaries and eutectic regions. Therefore, in order to design the microstructure of composites, interaction of nano-particles with an advancing solid-liquid interface needs to be studied in composites.

For a given particle size, some research [7-9] calculated a critical velocity of the solidification front to push the particles by the solid-liquid interface, which is the solidification velocity above which particles are engulfed by the interface and below which they are pushed. It is clear that particle expulsion or engulfment is a complicated phenomenon. Thus, a model for calculating critical velocity should take into account all of the different forces acting on the particles. Finally, an expression for critical velocity can be obtained by balance of these forces.

One of the earliest models for calculation of critical velocity is the one developed by Uhlmann et al. (UCJ) [10] that introduced the viscous drag force and the repulsive force induced by the interfacial energy change. Agreement with experiment results depends principally on choice of exponent n and diffusion coefficient. Based on the

UCJ model, Stefanescu et al. [11] suggested inclusion of the effect of thermal conductivity mismatch. After that, Shangguan et al. [12] extended the Stefanescu et al. model to accurately determine local perturbation of front morphology (SAS). Finally, Stefanescu et al. [13] modified the SAS model, determining that model accuracy depends on calculation of the interfacial energy change. Several particle-pushing models developed for the critical velocity prediction are summarized in Table 1, where one may observe that the critical velocity calculated by these models is an inverse function of particle radius. The preceding result indicates that critical velocity increases with reduction of particle size. Thus, smaller particles have a higher tendency to be pushed rather than engulfed. Nevertheless, these tabulated equations were developed for micron-sized particles; whether they are applicable to nano-particles remains unclear. Recently, Schultz et al. [4] discussed qualitatively the interaction between solid-liquid interface and nano-particles. Thus, a model is needed to calculate the critical velocity for nano-particles.

Particles pushed by the solid-liquid interface affect the temperature and solute gradient ahead of the solidification front, disturbing the grain growth and reforming the interface. Some research [14-16] found that solute concentration between the particle and the interface varies when a particle approaches the interface. The variation in the solute concentration between the particles and the interface leads to the difference in the interface growth velocities, which influences the interface shape behind the particles. Therefore, it is necessary to analyze the influence of solute concentration distributions behind the particles and away from the particles on growth velocity of solid-liquid interface. However, the effect of particles ahead of the interface on interface shape has not been considered in numerical calculation of solute concentration distributions behind the particles and away from the particles.

Investigation of relation of distribution and clustering degree of nano-sized Al_2O_3 in Al7075 with the microstructure of alloy would therefore be valuable and make the fabrication of as-cast composites with effective particle dispersion and superior mechanical properties more possible. The aim of this study is to establish a model for calculating the critical interface velocity for nano-particle pushing and to discuss

influence of the nano-particles present ahead of solidification front on interface shape. The experimental results were validated by the prediction of the model.

2. Experimental methods

Nano-sized α -Al₂O₃ (Al₂O_{3np}) was used as reinforcement of composites, which is 99.9% pure and has an average particle size of 80 nm (Guanye, China). Magnesium powders (99.9% pure, average particle size of 58-75 μ m) were used as wetting agent (Xilong Chemical, China). Aluminum alloy (Al7075) was used as the matrix, which chemical composition (wt.%) consists of Si = 0.22, Fe = 0.22, Cu = 1.45, Mn = 0.3, Mg = 2.1, Zn = 5.23, Ti = 0.16, Cr = 0.23, and balance as Al (Chinalco).

Al₂O_{3np} was specially made before fabrication of the composites, in which the particles were subjected to pre-dispersion in an ultrasonic bath, drying in a rotary vacuum evaporator, calcination at 540 °C for 3h, then mixing with magnesium powders. Al₂O_{3np} and magnesium powders were thoroughly mixed in a planetary ball milling machine at a constant rotation speed of 100 rpm for 30 min, in an argon gas atmosphere. The amount of Mg in the composite powder gives rise to the addition of 1.0 wt.% Mg to the melt.

In a clay-graphite crucible, Al7075 was melted using a resistance furnace under argon gas for protection. With the melt under ultrasonic vibration, the specially-made Al₂O_{3np}, wrapped in aluminum foils, was added to the melt at a rate of 0.3 g/min, whereupon the melt temperature was raised to 800 °C. To promote macroscopic dispersion of nano-particles during the addition of composite powders, the melt was ultrasonically vibrated at 1 kW and a frequency of 10 kHz. In order to obtain a full, microscopic dispersion of nano-particles in the melt after addition was complete, the ultrasonic process was carried out at 1 kW and 20 kHz for 10 min. Predetermined quantities of Al₂O_{3np} (0.5, 1.0, 1.5, 2.5 wt.%) were added to the melt. To avoid titanium contamination and adhesion of molten metal, the ultrasonic probe was coated with zirconia. The composite slurry after ultrasonic treatment was poured into a stainless crucible, which was preheated to 550-600 °C. Then, the composite slurry was allowed to cool in a quiescent fashion to a temperature of 700 °C. When the

appropriate temperature was reached, the molten materials were cast into a steel mold. To record the temperature and subsequently quantify the local solidification time, t_s , in the steel mold, a thermoelectric couple was placed in the alloy melt (20 mm from the bottom of cavity). At the given location, specimens were cut for metallographic examination. To evaluate the wettability of the above mixture powders by the molten alloy, some melts taken from the stainless crucible were used for testing by means of a self-made device equipped with digital camera. The schematic diagram of the experiment is shown in Fig.1.

Microstructural examination was performed by optical microscopy (OM, Nikon eclipse, MA-200), scanning electron microscope (SEM, Tescan, Vega3) and transmission electron microscope (TEM, Jeol, JEM-2100). Optical microstructures of the as-received composites were examined using the metallographic microscope after being etched by a 0.5 vol.% hydrofluoric acid (HF) water. To observe distribution of nano-particles and interface structure, microscopic examinations were carried out via the environment scanning electron microscope, equipped with X-ray mapping system.

3. Results and discussion

3.1 Particle distribution and grain size

Fig. 2 shows SEM micrographs of nano-particles distribution in the as cast composite containing 1.5 wt.% $\text{Al}_2\text{O}_{3\text{np}}$. As can be seen in Fig. 2a, few large aggregates of nano-particles are engulfed inside the grains. SEM morphologies under high magnification of objects in Fig. 2a are depicted in Fig. 2b and c, where the medium-sized aggregates of nano-particles are pushed toward final solidification regions, finally locating in the grain boundary (Fig. 2b), and individual $\text{Al}_2\text{O}_{3\text{np}}$ is uniformly distributed inside the grains (Fig. 2c). Fig. 3 shows a bright field TEM image of dispersion of individual $\text{Al}_2\text{O}_{3\text{np}}$ in the grains and SAD pattern of $\text{Al}_2\text{O}_{3\text{np}}$ phase. It is clearly seen that individual nano-particles are dispersed in the matrix. The TEM work provided further confirmation of the $\text{Al}_2\text{O}_{3\text{np}}$ oxide in the grains.

Sauter et al. [17] and Liu et al. [18] reported that ultrasonic frequency is inversely proportional to vibrational displacement amplitude at a constant acoustic pressure.

During the addition of particles, ultrasonic waves at low frequency and high amplitude destroyed weak bonds in large aggregates of $\text{Al}_2\text{O}_{3\text{np}}$, due to the alternating shear stress induced by ultrasonic vibration, which results in the macroscopic dispersion of particles. Subsequently, the nonlinear implosive impact produced by transient cavitations caused fatigue rupture of Van der Waals attractive forces between nano-particles at 20 kHz so that individual nano-particles and/or small nano-particle aggregates can be exfoliated from conglomerates of nano-particles.

Fig. 4 shows optical micrographs of the as cast composites. The mean grain size as a function of particle concentration, obtained in the experiment, is shown in Fig. 5. A significant decrease in grain size was achieved by the addition of $\text{Al}_2\text{O}_{3\text{np}}$, as shown in Fig. 5. In the received composites, the addition of 1.5 wt.% $\text{Al}_2\text{O}_{3\text{np}}$ reduced the grain size by approximately 74%, while further addition of nano-particles had little effect on grain size and even promoted a coarsened grain (Figs. 4 and 5). Increased addition amount of particles accelerates nano-particle clustering such that nano-particles are not effectively dispersed by ultrasonic processing and are easily engulfed by solidification front, which significantly weakens the influence of nano-particle additions on grain refinement. However, the medium sized aggregates of nano-particles pushed toward grain boundaries affect the solute and temperature gradient at the solidification front [4, 6], which restricts the grain growth, accordingly resulting in finer grains.

3.2 Calculation of solidification velocity

Fig. 6 shows the schematic diagram of static growth of spherical grain in the presence of nano-particles. In this study, assuming that the grain shape is spherical, the solid-liquid interface advances radially from the center toward the grain envelope within each sphere, finally stopping at its measured size. Therefore, the solidification velocity can be calculated by the following equation:

$$V = \frac{d_{avg}}{2t_s} \quad (1),$$

where, d_{avg} is the mean grain diameter size and t_s is the local solidification time obtained from the temperature acquisition instrument. In order to ensure the validity

of the calculated solidification velocity, the several points should be considered. Since the time required for the tip to reach the grain envelop is much smaller than t_s , the actual velocity of primary dendrite tip is much greater than the calculation value obtained by Eq. (1). The measured t_s is the time required for a dendrite arm to coarsen and for residual liquid among interdendrites to solidify. Calculation of the solidification velocity is also affected by other factors, such as grain impingement and introduction of external forces, which may limit free growth of the grain. Thus, the calculation result obtained through Eq. (1) yields a higher velocity.

To obtain a solidification velocity close to actual conditions, a modified equation should be established. In Fig. 6, V_1 represents the velocity of a primary dendrite tip and V_2 is the velocity perpendicular to the tip growth direction, that is, dendrite arm coarsening takes place during t_s . Breer et al. [19] and Bouchard and Kirkaldy [20] reported that the ratio of the velocity of primary dendrite tip to that of the dendrite arm coarsening is in the range of 3-5. In this study, an average value for V_1/V_2 of 4 was assumed for calculation of solidification velocity. The solidification velocity is controlled by V_2 , since V_1 is much larger than V_2 , thus the modified equation, V_{mod} , can be expressed by:

$$V_{mod} = \frac{d_{avg}}{8t_s} \quad (2).$$

The solidification velocity calculated by Eq. (2), local solidification time and average grain diameter are listed in Table 2, which demonstrate the influence of added nano-particles on the solidification velocity. In a constant ultrasonic power (1 kW), the number of individual nano-particles dispersed in the matrix would decrease as the addition amount of Al_2O_{3np} was increased due to the limitation of ultrasonic dispersion of nano-particles in the alloy melts and the high viscosity induced by high-content Al_2O_{3np} , accompanied by an increase of medium-sized nano-particle aggregates pushed toward grain boundaries. Further grain growth is consequently hindered, leading to lower solidification velocity. The influence of particle pushing on grain refinement weakens with increased concentration of nano-particles in the melt, due to formation of larger aggregates of nano-particle, which results in higher

solidification velocity.

3.3 Critical velocity model prediction

Under no- or low-melt convection during crystal growth, there is a critical velocity, above which particles are engulfed by the solidifying front, and below which they are pushed. As described by Agalotis et al. [21], the physical circumstance under investigation consists basically of a spherical particle immersed in molten alloy and an advancing solid-liquid interface towards the particle (Fig. 7). In order to simplify the problem, the effects of gravity, lift force produced by the velocity gradient of the melt, as well as viscous force applied by the melt flow surrounding the particle are neglected, while only two forces acting on the particle are considered: repulsion and drag force.

Result of competition between repulsive (F_r) and drag forces (F_d) determine whether a particle is pushed or engulfed. The particle is in an equilibrium state when F_r is equal to F_d , while the corresponding distance between the particle and the interface is the equilibrium separation distance in steady state of pushing (h_{eq}). Sharp and Adrian [22] and Travis et al. [23] reported that trapping conditions are obtained when the equilibrium separation distance reaches a minimum value of $h_0 = 1 \times 10^{-8}$ m. It is assumed to be a minimum layer thickness of a melt that may be considered as a liquid. Accordingly, when separation distance is larger than h_0 , a steady state of pushing is achieved, though when that distance is smaller than h_0 , the particle is engulfed since the necessary flow for solidification is not possible.

In order to deduce a critical velocity formula, individual or small aggregates of nano-particles, medium sized aggregates and large aggregates are treated as a single particle type of different sizes. The repulsive force from interfacial energy change can be expressed as [24]:

$$F_r = 2\pi r \Delta\gamma \left(\frac{a_0}{a_0 + h} \right)^2 k^* \quad (3),$$

where, r is the particle radius, $\Delta\gamma$ is the interface energy change, a_0 is the interatomic distance, h is the separation distance between particle and interface and k^* is the interface shape factor. In many cases, this factor is considered as the ratio of the

thermal conductivity of the particle to that of the melt. The interfacial energy change, which induces the repulsive force, can be described by the following equation [8-9]:

$$\Delta\gamma = \Delta\gamma_0 \left(\frac{h_0}{h} \right)^n \text{ with } \Delta\gamma_0 = \gamma_{PS} - \gamma_{PL} - \gamma_{LS} \quad (4),$$

where, the subscripts P , S and L refer to the ceramic particle, solid and liquid phases, respectively, while $n = 4$ [8-9]. Substituting Eq. (4) into Eq. (3), the repulsive force can be expressed as:

$$F_r = 2\pi r \Delta\gamma_0 \left(\frac{h_0}{h} \right)^4 \left(\frac{a_0}{a_0 + h} \right)^2 k^* \quad (5).$$

During solidification, a drag force is induced by flow of liquid around the particle, which resists movement of the particle away from the advancing interface. Based on a modified Stocks' law, the drag force is given by:

$$F_d = 6\pi\eta V_{\text{int}} \frac{r^2}{h} k^{*2} \quad (6),$$

where, V_{int} is the solidification front velocity and η is the dynamic viscosity of the melt. Balancing the repulsive force and the drag force yields an equilibrium solidification velocity, V_{eq} thus:

$$V_{\text{eq}} = \frac{1}{3} \frac{\Delta\gamma_0 h_0^4 a_0^2}{\eta r k^* h^3 (a_0 + h)^2} \quad (7).$$

When $h = h_0$, the critical velocity for steady state of pushing, V_{cr} , can be obtained by:

$$V_{\text{cr}} = \frac{1}{3} \frac{\Delta\gamma_0 h_0^4 a_0^2}{\eta r k^* (a_0 + h_0)^2} \quad (8).$$

It can be seen in Eq. (8) that the critical velocity for particle pushing by the solidification front increases with the reduction of particle size, which suggests that smaller particles have a greater tendency to be pushed rather than engulfed. However, single nano-particles are uniformly distributed inside the grains of the composites (Fig. 2c), which fact indicates that individual or small aggregates of nano-particles can be engulfed by the solidification front. Thus, the model for explaining the distribution of ultra-fine particles includes limitations.

The effect of Brownian motion of liquid particles on large solid particles in the melt

can be disregarded. Even so, the effect of collisions between the liquid particles and the ultra-fine particles can impart a significant change in direction of movement. The force produced due to collision of molecules is oftentimes called Brownian force. The force that causes particle diffusion that is equal to the Stokes-Einstein dispersion is [25]:

$$\vec{F}_{Br} = \vec{C} \sqrt{\frac{12\pi k_B T r \eta}{\Delta t}} \quad (9),$$

where, $\vec{C}$ is a random vector and assumed as $\vec{C}=1$, Δt is the time interval of action of the Brownian force, k_B is the Boltzmann constant (1.38054×10^{-23} J/K) and T is the absolute temperature.

Schultz et al. [4] reported that at some critical particle size, Brownian force is equal to buoyancy force which is produced due to the difference in density between the particles and the melt. The equilibrium equation is given by:

$$F_{Bu} = \frac{4}{3} \pi |\rho_P - \rho_L| r^{*3} g = \sqrt{\frac{12\pi k_B T r^* \eta}{\Delta t}} \quad (10).$$

Finally the critical radius of the particles (r^*) is obtained from Eq. (10) as:

$$r^* = \left(\frac{27}{4} \frac{k_B T \eta}{\pi \Delta t (\rho_P - \rho_L)^2 g^2} \right)^{\frac{1}{5}} \quad (11),$$

where, ρ_P is the density of Al_2O_3 particles (4050 kg/m^3), ρ_L is the density of the alloy melt (2700 kg/m^3) and g is the gravitational acceleration (9.8 m/s^2). When particles are below the critical radius, the drag force is significantly affected by Brownian force. Meanwhile, for the ultra-fine particles, the effect of the difference in thermal conductivity between the particles and the melt on the interface shape is negligible. Hence, the possible expression of the drag force, making use of Stokes' law under the regime of Brownian motion, can be given by [4]:

$$F_d = 6\pi r \eta V_{in} \left(1 + e^{\pi^2 \left(1 - \frac{r}{r^*} \right)} \right) \quad (12).$$

In addition, the disjoining pressure is mainly caused by the van der Waals force in the

particle/interface gap for the ultra-fine particles, as described by Eq. (13) [9]:

$$F_r = \frac{\pi B r}{h^2} \quad (13),$$

where, B is the Hamaker constant between particle and interface. Balancing repulsive force and drag forces, we get an equilibrium solidification velocity for pushing of ultra-fine particles, V_{eq} as:

$$V_{eq} = \frac{1}{6} \frac{B}{\eta h^2} \left(1 + e^{\pi^2 \left(1 - \frac{r}{r^*} \right)} \right)^{-1} \quad (14).$$

When $h = h_0$, the critical velocity for steady state of pushing is obtained as V_{cr} :

$$V_{cr} = \frac{1}{6} \frac{B}{\eta h_0^2} \left(1 + e^{\pi^2 \left(1 - \frac{r}{r^*} \right)} \right)^{-1} \quad (15).$$

When nano-particles are beyond the critical radius, it can be seen from Eq. (8) that the critical interface velocity for particle pushing increases with the decrease of particle size. The particles may be pushed by the solid-liquid interface and then act as barriers to grain growth. It should be expected that as particle size reduces for the same volume addition of particles, the growth restrictions imposed by particle pushing would be enhanced. Whereas for large aggregates of nano-particles, they can be easily engulfed by the solidification front and thus distributed inside grains or in the interdendrite due to its low critical interface velocity. For nano-particles below the critical radius, it can be seen from Eq. (15) that the critical interface velocity for particle pushing decreases as particle size is reduced, which indicates that the particles are with a low critical interface velocity and accordingly engulfed by the interface. Thus, by using the rapid solidification rates, such as squeeze cast, the use of copper mould, etc., many of ultra-fine particles would be engulfed by the interface, which contributes to improvement of the mechanical properties of composites. Meanwhile, by controlling the size of nano-particle clustering in the matrix and the solidification velocity, the required distribution of nano-particles in the alloys could be obtained.

To calculate the critical velocity for particle pushing, a number of material parameters

are needed, the most important of which are the interface energy change and the Hamaker constant. The calculation of the parameter $\Delta\gamma_0$ was done as follows. The solid-liquid interface energy, γ_{LS} , was calculated using Turnbull-Vonnegut theory [26]. According to the $\text{Al}_2\text{O}_{3\text{np}}$ -gas interface energy value calculated by Sun et al. [27] and the equation suggested by Sen et al. [8], the $\text{Al}_2\text{O}_{3\text{np}}$ -solid phase interface energy, γ_{PS} , was established. The $\text{Al}_2\text{O}_{3\text{np}}$ -liquid interface energy, γ_{PL} , was calculated from Young's equation. The contact angle (θ) was measured by the sessile drop experiment (102°). The liquid-gas interface energy, γ_{LG} , was calculated via the equation reported by Kaptay [28]. The relevant thermodynamic values used for the $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$ system were taken from the Data Book [29]. The values obtained for γ_{LS} , γ_{PS} and γ_{PL} were 0.11, 2.71 and 2.07 J/m², respectively. In consideration of the effect of Mg on lowering interface energy, a lower Hamaker constant value of 1×10^{-21} , was assumed, allowing the model established in this work to agree reasonably well with experiment results. The parameters used to calculate the critical velocity are summarized in Table 3. According to the parameter values, a critical radius of 2.77×10^{-6} m is obtained, or $r^* = 2.77 \times 10^{-6}$ m. In the model described by Eq. (15), the critical velocity for steady state of pushing is very low, indicating that ultra-fine particles are easily engulfed by the advancing solidification front, which agrees more closely with the experiment results. When the particles are above the critical radius, the model established through Eq. (15) cannot be applied to explain distribution of nano-particles in the matrix, but a model based on Eq. (8) can.

For particle radii ranging from 50 nm - 20 μm , the equilibrium separation distances versus velocity are shown in Fig. 8, while Fig. 8a reveals that all the lines are parallel and linear at small equilibrium distances, and that the lines start to curve towards the abscissa with the decrease of the equilibrium solidification velocity. The described difference is due to use of a modified Stocks equation to evaluate drag force, which is generally used for small separation distances between particle and interface. The results are consistent with the previous work reported by Agaliotis et al. [30]. Also, Fig. 8a clarifies that the equilibrium solidification velocity increases with the reduction of particle size at a constant separation distance. For ultra-fine particles,

however, variation of velocity with particle size presents an inverse trend (Fig. 8b). This is mainly attributed to different particle movement control mechanisms as described above.

As previously described, the critical velocity for steady state of pushing occurs at the point where line intercepts the abscissa, which corresponds to a minimum separation distance of 1×10^{-8} m.

Fig. 9 shows the critical velocity as a function of particle size, which is a result of the critical velocity for particle pushing and is quantitatively shown for a given solidification velocity (2.18×10^{-6} m/s). For particles below approximately 36% of the critical radius, the critical velocities for particle pushing are four orders of magnitude lower than those obtained by micron particles, meanwhile they are far below the given velocity, which suggests that Brownian motion effects are more significant than any other effects for very small particles, and that particles below the critical radius are engulfed rather than pushed. For particles ranging 2.77-10 μm , the critical velocities are higher than the given velocity, thus leading to the steady state of pushing. In addition, the critical velocity is demonstrably lower than the given velocity when particles are above 10 μm , indicating that the particles are engulfed by an advancing solidification front. Calculation results obtained by the above models agree reasonably well with the experimental results (Fig. 2).

There is a consideration that is involved in grain refinement by particle pushing concerning the effect of lower thermal conductivity of particle on solute and temperature gradients ahead of the solidification front, which restricts grain growth.

3.4 Effect of particle pushing on grain growth

During solidification of alloy melts, latent heat and solute diffusion are away from solid-liquid interface. Since the particles are far from the interface, the interface movement is not affected by the presence of particles. However, the interface velocity for steady particle pushing increases when particles approach the interface, as shown in Fig. 8, thus leading to unstable interface movement. Fig. 10 presents the schematic diagram of solute concentration profile ahead of the interface. When the particle (an agglomerate of nano-particles) is present ahead of the interface, the interface velocity

can be divided into two parts, V_1 at region 1 and V_2 at region 2, where the velocity at the interface region 1 is unrelated to the particle, and at the interface region 2 it is affected by the particle. As shown in Fig. 10, the concentration distribution ahead of the interface yields the difference between adjacent interface regions, due to solute accumulation induced by the presence of particle. To determine the effect of presence of particle on the velocity at interface regions 1 and 2, the concentration distribution ahead of the interface is needed.

Concentration distribution depends on the concentration variations induced by: (1) solute diffusion and (2) the movement of solute concentration profile with the interface velocity. Thus, the governing equation of solute diffusion at interface region 1 under steady state conditions can be expressed by the following expressions, which was reported by [31]:

$$D \frac{\partial^2 C}{\partial y^2} + V_1 \frac{\partial C}{\partial y} = 0 \quad (16),$$

where, D is the diffusion coefficient of solute and V_1 is the interface velocity at the region 1. The boundary conditions are given as follows: $C = C_0/k_0 = C_1$ at $y = 0$ and $C = C_0$ at $y = \infty$. So the solute concentration at interface region 1 is expressed by:

$$C_1(y) = C_0 \left(1 + \frac{1 - k_0}{k_0} e^{-\frac{V_1}{D} y} \right) \quad (17),$$

where, k_0 is the equilibrium distribution ratio ($k_0 < 1$) and C_0 is the initial weight fraction of the alloy element. According to the mass balance at interface region 1, the interface velocity at region 1 is given by [31]:

$$V_1 = \frac{-Dk_0}{C_0(1 - k_0)} G_1 \quad (18),$$

where, G_1 is the gradient of solute concentration at the interface region 1. When a particle is present within solute diffusion length, solute accumulation will occur due to the presence of the particle, finally affecting diffusion of the solute. According to Eq. (16), and taking into consideration the effect of particle size on concentration distribution, the governing equation of solute diffusion at interface region 2 is given by:

$$D \frac{\partial^2 C}{\partial x^2} + D \frac{\partial^2 C}{\partial y^2} + \frac{V_2 \partial C}{\partial y} = 0 \quad (19)$$

where V_2 is the interface velocity at the region 2. The boundary conditions are given by: $C = C_0/k_0 = C_1$ at $x = 0, y = 0$; $C = C_h$ at $x = 0, y = h$ ($h < h'$); and $C = C_1$ at $x = r, y = 0$, where h' is the solute diffusion length ($2D/V$) and C_h is the solute concentration at h . Substitution of the boundary conditions into Eq. (19) yields the solute concentration behind the particle under steady state conditions:

$$C_2(x, y) = C_1 - (C_1 - C_h) \left(1 - e^{-\frac{V_2 y}{D}} \right)^{-1} \left(1 - e^{-\frac{V_2 y}{D}} \cos\left(\frac{2\pi}{r} x\right) \right) \quad (20).$$

According to mass balance theory, the interface velocity at region 2 is given by:

$$V_2 = \frac{-Dk_0}{C_0(1 - k_0)} G_2 \quad (21)$$

where G_2 is the gradient of solute concentration at interface region 2.

Du et al. [32] investigated the diffusion coefficients of several transition elements (Ti, Cr, Mn, Fe, Ni, Cu, and Zn) and a few non-transition elements (Mg, Si, and Ga) in liquid Al, and found that the diffusion coefficient of Zn is three orders of magnitude lower than that of Mg ($D_{Zn} = 2.75 \times 10^{-9} \text{ m}^2/\text{s}$). Thus, the diffusion coefficient of solute elements in the alloy melts is approximately equal to that of Zn in the melts. Yang et al. [33] reported a DSC result where k_0 is around 0.32. The solute concentration at interface regions 1 and 2 was numerically simulated. Fig. 11 shows the simulated concentration distribution ahead of the interface, wherein the particle hindered diffusion of the solute from the solid-liquid interface, leading to solute accumulation in the gap between particle and interface, which indicates that the solute concentration gradient at region 2 is lower than that at region 1 ($G_2 < G_1$). Moreover, Fig. 11b and c evidence that the particle size has a great influence on concentration distribution at interface region 2, which leads to unstable solute diffusion. From Eq. (20), it can be deduced that the effect of particles on the concentration distribution shrinks with the increase of separation distance. In addition, Fig. 11b shows that there is a lower solute concentration near the $r/2$, for which the reason is not completely clear and further investigation is needed.

Fig. 12 shows SEM-EDS images of $\text{Al}_2\text{O}_{3\text{np}}/7075$ composite slurry at 620 °C quenched in water. The interface's cellular structure manifests clearly, as arrowed in Fig. 12a. The high magnification of a cellular interface with grooves is shown in Fig. 12b. The EDS analysis results of different positions in the groove are shown in Fig. 12c-e. At point 1, the segregation of solute occurred during solidification led to the high concentration of Cu, Mg and Zn in the groove region (76.23 wt.% Al, 12.67 wt.% Zn, 3.50 wt.% Mg, 7.60 wt.% Cu). At point 2, the alloy elements decreased in content (70.44 wt.% Al, 11.10 wt.% Zn, 4.25 wt.% Mg, 5.97 wt.% Cu). However, at the solidification front, the oxygen element concentration yielded 15.04 wt.%, and the zinc, magnesium and copper contents were still higher than the average level of chemical composition in the Al7075 alloy, which indicate that the Al_2O_3 nano-particles are located in the eutectic regions ahead of the interface (66.77 wt.% Al, 9.01 wt.% Zn, 3.47 wt.% Mg, 4.10 wt.% Cu, 15.04 wt.% O).

The formation of the cellular structure mainly relates to difference of interface velocity between regions 1 and 2. Eqs. (18) and (21) indicate that the difference in solute gradient between regions 1 and 2 leads to the difference in interface velocity between the two regions ($V_2 < V_1$), which contributes to bifurcation of the interface, in turn resulting in formation of a concave interface behind the particle. On the other hand, the interface region 1 faces greater super-cooling compared to region 2 due to its faster interface velocity, meanwhile removes solute toward surrounding melts continually. The solute concentration in the cavity of interface region 2 increases faster than that ahead of interface region 1, since a concave interface shape prevents the solute from making outward diffusion. In addition, the fast growth of interface region 1 promotes further accumulation of solute behind the particle. Nevertheless, the accumulation of solute reduces the liquidus temperature and super-cooling degree of melt in the gap between particle and interface, thus restricting transverse growth of the interface at region 1, and leading finally to formation of a groove which consists of eutectic phases.

The tip of the interface at region 1 cannot grow freely in the melt. According to Hu [31], the liquidus temperature gradient at interface region 1 is given by:

$$dT_1 = -m \frac{V_1}{D} \frac{C_0(1-k_0)}{k_0} \quad (22),$$

where, m is the slope of the liquidus ($m < 0$). In order to remain steady state during solidification, it is well known that a growing grain exists a transforming tendency from dendrite to global grain, due to the grain's lower gas/solid interface energy. Dong et al. [34] discussed the effect of interface curvature on liquidus temperature gradient, and found that this tendency hindered the growth of dendrites. Thus, the liquidus temperature gradient at interface region 1 can be modified as follows:

$$dT_{1\text{mod}} = -\left(m \frac{V_1}{D} \frac{C_0(1-k_0)}{k_0} - \frac{\Gamma k_0 V_1^2}{D^2} \right) \quad (23)$$

where $\Gamma = \frac{\gamma_{SL}}{\Delta S_f}$, Γ is the Gibbs-Thomson coefficient and ΔS_f is the entropy of

fusion per unit volume. As is evident, constitutional super-cooling favors interface growth at region 1. However, the interface cannot grow freely, due to a limiting constitutional super-cooling range. As well, the hindering effect of interface curvature on growth of dendrites also prevents growth of the interface at region 1.

Therefore, the constitutional supercooling of local melts and the solute pileup behind the particle lead to bifurcation of the interface, finally promoting formation of the cellular interface, as shown in Fig. 12.

Whether the particle is engulfed by the interface depends on solidification velocity. When solidification velocity is less than critical velocity, particles are still present ahead of the interface even though the formation of a concave interface occurs. Meanwhile, if the width of groove is less than particle size, the engulfment of particle is difficult to occur, facilitating segregation of the particle in grain boundary region. The effect of actual temperature gradient ahead of the interface on interface shape can not be neglected. The coupled effect of the actual temperature gradient and the liquidus temperature gradient at the interface is the subject for further study in our group.

4. Conclusions

(1) Based on microstructure analysis, it was found that the resulting microstructures of composites depended on the distribution and size of $\text{Al}_2\text{O}_{3\text{np}}$ clustering and that the addition of $\text{Al}_2\text{O}_{3\text{np}}$ caused refined grains. Compared to the matrix alloy, the grain size of the as cast composite with 1.5 wt.% $\text{Al}_2\text{O}_{3\text{np}}$ was decreased by 74%. The grain refinement was attributed to particle pushing mechanisms.

(2) Solidification velocity was influenced by addition of nano-particles. Particles pushed by the solidification front hindered the further growth of grains, leading to reduced solidification velocity. When excess nano-particles were added to the melt, the influence of particle pushing on grain refinement was weakened by larger aggregates of nano-particles, resulting in increased solidification velocity.

(3) According to the established particle pushing model, it was found that for particles below approximately 36% of the critical radius, the critical interface velocities were four orders of magnitude lower than those obtained by micron particles and were far below the measured solidification velocity, suggesting that smaller particles are easily engulfed by the interface rather than pushed. The results obtained by the model agree reasonably well with the experimental results.

(4) The nano-particles present ahead of the solidification front led to growth velocity difference between the interfaces with and without the particles. Constitutional super-cooling of local melts and solute pileup behind the particle caused splitting of the interface, finally promoting formation of a cellular interface.

Acknowledgments

Authors express their gratitude to the National Science Foundation of China (51364035), Ministry of Education Tied up with the Special Research Fund for the Doctoral Program for Higher School (20133601110001), Production and Teaching and Research Cooperation Plan of Nanchang Non-party Experts and Doctor (2012-CYH-DW-XCL-002), and Innovation Program of Postgraduate of Jiangxi Province (YC2014-B003) for financial support.

References

[1] Yar AA, Montazerian M, Abdizadeh H, Baharvandi. Microstructure and mechanical properties

- of aluminum alloy matrix composites reinforced with nano-particle MgO. *J Alloys Compd* 2009; 484: 400-404.
- [2] Sajjadi SA, Ezatpour HZ, Parizi Torabi M. Comparison of microstructure and mechanical properties of A356 aluminum alloy/ Al_2O_3 composites fabricated by stir and compo-casting processes. *Mater Des* 2012; 34: 106-111.
- [3] Chen XH, Yan H. Fabrication of nanosized Al_2O_3 reinforced aluminum matrix composites by subtype multifrequency ultrasonic vibration. *J Mater Res* 2015; 30: 2198-2209.
- [4] Schultz BF, Ferguson JB, Rohatgi PK. Microstructure and hardness of Al_2O_3 nanoparticle reinforced Al–Mg composites fabricated by reactive wetting and stir mixing. *Mater Sci Eng A* 2011; 530: 87-97.
- [5] Yang Y, Lan J, Li XC. Study on bulk aluminum matrix nano-composite fabricated by ultrasonic dispersion of nano-sized SiC particles in molten aluminum alloy. *Mater Sci Eng A* 2004; 380: 378-383.
- [6] Su H, Gao WL, Feng ZH, Lu Z. Processing, microstructure and tensile properties of nano-sized Al_2O_3 particle reinforced aluminum matrix composites. *Mater Des* 2012; 36: 590-596.
- [7] Han Q, Hunt JD. Particle pushing: critical flow rate required to put particles into motion. *J Cryst Growth* 1995; 152: 221-227.
- [8] Sen S, Dhindaw BK, Stefanescu DM, Catalina A, Curreri PA. Melt convection effects on the critical velocity of particle engulfment. *J Cryst Growth* 1997; 173: 574-584.
- [9] Youssef YM, Dashwood RJ, Lee PD. Effect of clustering on particle pushing and solidification behaviour in TiB_2 reinforced aluminum PMMCs. *Composites A* 2005; 36: 747-763.
- [10] Uhlmann DR, Chalmers B, Jackson KA. Interaction between particles and a solid-liquid interface. *J Appl Phys* 1964; 35: 2986-2993.
- [11] Stefanescu DM, Dhindaw BK, Kacar SA, Moitra A. Behavior of ceramic particles at the solid/liquid metal interface in metal matrix composites. *Metall Trans A* 1988; 19: 2847-2855.
- [12] Shanguan D, Ahuja S, Stefanescu DM. An analytical model for the interaction between an insoluble particle and an advancing solid/liquid interface. *Metall Trans A* 1992; 23: 669-680.
- [13] Stefanescu DM, Juretzko FR, Catalina A, Dhindaw BK, Sen S, Curreri PA. Particle engulfment and pushing by solidifying interfaces. II. Microgravity experiments and

theoretical analysis. Metall Mater Trans A 1998; 29: 1697-1706.

- [14] Kim JK, Rohatgi PK. An analytical solution of the critical interface velocity for the encapsulating of insoluble particles by a moving solid/liquid interface. Metall Mater Trans A 1998; 29: 351-358.
- [15] Rempel AW, Worster MG. The interaction between a particle and an advancing solidification front. J Cryst Growth 1999; 205: 427-440.
- [16] Hadji L. Modelling and asymptotic analysis of particle-interface interaction. Math Comput Model 2002; 36: 147-156.
- [17] Sauter C, Emin MA, Schuchmann HP, Tavman S. Influence of hydrostatic pressure and sound amplitude on the ultrasound induced dispersion and de-agglomeration of nanoparticles. Ultrason Sonochem 2008; 15: 517-523.
- [18] Liu ZW, Han QY, Li JG, Huang WD. Effect of ultrasonic vibration on microstructural evolution of the reinforcements and degassing of in situ $\text{TiB}_{2p}/\text{Al-12Si-4Cu}$ composites. J Mater Process Technol 2012; 212:365-71.
- [19] Greer AL, Bunn AM, Tronche A, Evans PV, Bristow DJ. Modelling of inoculation of metallic melts: application to grain refinement of aluminium by Al-Ti-B. Acta Mater 2000; 48: 2823-2835.
- [20] Bouchard D, Kirkaldy JS. Prediction of dendrite arm spacings in unsteady- and steady-state heat flow of unidirectionally solidified binary alloys. Metall Mater Trans B 1997; 28: 653-663.
- [21] Agaliotis EM, Schvezov CE, Rosenberger MR, Ares AE. Numerical model study of the effect of interface shape on particle pushing. J Cryst Growth 2012; 354: 49-56.
- [22] Sharp KV, Adrian RJ. Transition from laminar to turbulent flow in liquid filled microtubes. Exp Fluides 2004; 36: 741-747.
- [23] Travis K, Tood B, Evans D. Departure from Navier-Stokes hydrodynamics in confined liquids. Phys Rev E 1997; 55: 4288-4295.
- [24] Sen S, Curreri P, Kaukler WF, Stefanescu DM. Dynamic of solid/liquid interface shape evolution near an insoluble particle-an X-ray transmission microsocppy investigation. Metall Mater Trans A 1997; 28: 2129-2135.
- [25] Michaelides EE. Brownian movement and thermophoresis of nanoparticles in liquids. Int J Heat Mass Transfer 2015; 81: 179-187.

- [26] Xu R, Jing TF. Thermodynamics and kinetics of materials. Harbin Institute of Technology Press, Harbin, 2003: 164-177.
- [27] Sun JZ, Stirner T, Matthews A. Structure and surface energy of low-index surfaces of stoichiometric α -Al₂O₃ and α -Cr₂O₃. Surf Coat Tech 2006; 201: 4205-4208.
- [28] Kaptay G. A unified model for the cohesive enthalpy, critical temperature, surface tension and volume thermal expansion coefficient of liquid metals of bcc, fcc and hcp crystals. Mater Sci Eng A 2008; 495: 19-26.
- [29] Barin I. Thermochemical data of pure substances. VCH, Weinheim, 1995: 17.
- [30] Agaliotis E, Rosenberger MR, Schvezov CE, Ares AE. Numerical calculation of the drag force applied to particle pushing. J Cryst Growth 2008; 310: 1366-1370.
- [31] Hu HQ. Fundamentals of solidification. China Machine Press, Beijing, 1987: 65-100.
- [32] Du Y, Chang YA, Huang BY, Gong WP, Jin, ZP. Diffusion coefficients of some solutes in fcc and liquid Al: critical evaluation and correlation and correlation. Mater Sci Eng A 2003; 363: 140-151.
- [33] Yang B, Mao WM, Song XJ. Microstructure evolution of semi-solid 7075 Al alloy slurry during temperature homogenization treatment. Trans Nonferrous Met Soc China 2013; 23: 3592-3597.
- [34] Dong J, Cui JZ, Le QC, Lu GM. Liquidus semi-continuous casting, reheating and thixoforming of a wrought aluminum alloy 7075. Mater Sci Eng A 2003; 345: 234-242.
- [35] Parchovianský M, Galusek D, Švančárek P, Sedláček J, Šajgalík P. Thermal behavior, electrical conductivity and microstructure of hotpressed Al₂O₃/SiC nano-composites. Ceram Int 2014; 40: 14421-14449.
- [36] Meydani F, Saatci B, Özdemir M. Thermal conductivities of solid and liquid phase for pure Al, pure Sn and their binary alloys. Fluid Phase Equilib 2010; 298: 97-105.
- [37] Rogal L, Dutkiewicz J, Atkinson HV, Lityńska-Dobrzyńska L, Czeppe T, Modigell M. Characterization of semi-solid processing of aluminium alloy 7075 with Sc and Zr additions. Mater Sci Eng A 2013; 580: 362-373.
- [38] Sato M, Katsuno H, Suzuki Y. Ordering of Brownian particles from walls due to an external force. J Cryst Growth 2014; 401: 87-92.

Table captions

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Table 2 Calculated solidification velocity for Al7075 containing $\text{Al}_2\text{O}_{3\text{np}}$.

Table 3 Parameters used for calculations of critical velocity in $\text{Al}_2\text{O}_{3\text{np}}$ /Al alloy system.

Figure captions

Fig. 1. Schematic diagram of experiment.

Fig. 2 SEM micrographs of particle distribution in the composite with 1.5 wt.% $\text{Al}_2\text{O}_{3\text{np}}$: (a) lower magnification; (b) grain boundary and (c) grain inside.

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Fig. 9 Critical velocity as function of particle size: (a) ultra-fine particles; (b) larger particles.

Fig. 10 Schematic representation of the interaction between particle and interface and the solute profile at the interface.

Fig. 11 Solute concentration ahead of the interface: (a) interface region 1; (b) interface region 2, $h = 1 \times 10^{-7}$ m, $r = 5 \times 10^{-6}$ m; and (c) interface region 2, neglecting the effect of particle size on concentration distribution.

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Table 1 Summary of the models used for prediction of critical interface velocity.

Authors	Model	Dependence on particle radius
Uhlmann et al. [10]	$V_c = \left(\frac{n+1}{2} \right) \left(\frac{La_0\Omega D}{k_B T r^2} \right), n = 4-5$ <p>where L is latent heat of fusion and Ω is atomic volume</p>	$\frac{1}{r^2}$
Stefanescu et al. [11]	$V_c = \frac{\Delta\gamma_0 h_0}{6(n-1)\eta r} \left(2 - \frac{k_P}{k_L} \right), n = 2-7$	$\frac{1}{r}$
Shangguan et al. [12]	$V_c = \frac{\Delta\gamma_0 a_0}{3(n-1)k^* \eta r} \left(\frac{n-1}{n} \right)^n, n = 2-7$	$\frac{1}{r}$
Stefanescu et al. [13]	$V_c = \left(\frac{\Delta\gamma_0 a_0^2}{3\eta k^* r} \right)^{1/2}$	$\left(\frac{1}{r} \right)^{1/2}$
Kim and Rohatgi [14]	$V_c = \frac{a_0 \Delta\gamma_0}{18\eta} \left(\frac{\kappa r + 1}{r} \right), \kappa = 1/R_I$ <p>where R_I is interface radius</p>	$\frac{1}{r}$

Table 2 Calculated solidification velocity for Al7075 containing Al₂O_{3np}.

Al ₂ O _{3np} (wt.%)	t_s (s)	d_{avg} (μm)	v_{mod} (m/s)
0.5	5.0	152	3.8×10^{-6}
1.0	5.0	103	2.58×10^{-6}
1.5	5.0	87	2.18×10^{-6}
2.5	5.0	110	2.75×10^{-6}

Table 3 Parameters used for calculations of critical velocity in Al₂O_{3np}/Al alloy system.

Parameter	Unit	Value	Source
a_0		2.55×10^{-10}	[9]
$\Delta \gamma_0$	J/m ²	0.53	
k^*		0.125	[35-36]
η	Pa s	0.4	[37]
T	K	913	
Δt	s	1×10^{-3}	[38]
B		1×10^{-21}	[9]

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Nanoparticle solid-liquid flow models

$$V_{cr} = \frac{1}{3} \frac{\Delta\gamma_0 h_0 a_0^2}{\eta r k^* (a_0 + h_0)^2} \quad (r > 2.77 \mu\text{m})$$

and

$$V_{cr} = \frac{1}{6} \frac{B}{\eta h_0^2} \left(1 + e^{\pi^2 \left(\frac{1-r}{r} \right)^{-1}} \right) \quad (r \leq 2.77 \mu\text{m})$$

where $r^* = 2.77 \mu\text{m}$

Nano-particle distribution in grain

Nano-particle distribution along grain boundary

Nano-particle distribution in grain