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BROWNIAN MOTION EFFECTS ON THE PARTICLE SETTLING AND ITS APPLICATION TO SOLIDIFICATION FRONT IN METAL MATRIX COMPOSITES

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Abstract

Studying the interactions between the reinforcement particles and solidification front of metal-matrix composites (MMCs) and/or metal-matrix nanocomposites (MMNCs) synthesized using solidification processing is essential to understand the particle strengthening mechanism of these materials. Previous models describing such reinforcement particle and solidification front interactions predict that large particles will be engulfed by the solidification front while smaller particles and nanoparticles will be pushed. However, these models cannot explain the evidence in MMNCs produced by solidification processing that nanoparticles can indeed be engulfed and distributed throughout the material and are not necessarily concentrated in grain boundary or interdendritic regions. In this work, an analytical model of particle size effects on the particle settling due to gravity and the pushing/engulfment during solidification is described that accounts for both Stokes' law and Brownian motion. The model shows a clear transition from Stokesian- to Brownian-dominant behaviors of ultra-fine nano-sized reinforcement particles, which indicates that these fine particles may be engulfed rather than pushed by the solidification front.

Introduction

In theory, the incorporation of nano-sized reinforcements in metals and alloys will result in an Orowan-type strengthening mechanism where line defects are pinned by a uniform dispersion of particles within the grains, causing the dislocations to bow [0,0]. Proper activation of such Orowan-type strengthening is important as it does not reduce the ductility while it has a strong potential to increase the strength of composites. Other than Orowan-type strengthening, experimental evidence also shows that a significant degree of grain refinement (i.e., Hall-Petch strengthening) often occurs with additions of nano particles (NPs) [0-0]. The strengths of NP reinforced composites attained by researchers could thus be a result of dislocation pinning due to grain refinement, dispersed particles, or a combination of both [6].

Solidification processing has the potential to be one of the most economically viable methods of producing a high strength metal-matrix nanocomposite (MMNC) [1-7]. Casting of an MMNC where Orowan strengthening is dominant requires the dispersion of NPs in the liquid melt followed by the engulfment of the particles within the solidifying grains. This requires producing homogeneous distributions of NPs without agglomeration during solidification processing and is essential in attaining enhanced mechanical properties by the activation of Orowan-type mechanism. It is likely that MMNCs that show only grain refinement strengthening do not contain particles within the grains, but rather have high concentrations at grain boundaries and/or interdendritic regions as a result of their being pushed ahead of the solidifying grains. It is, therefore, important to understand the interactions between NPs and the solidification front and the subsequent particle pushing/engulfment phenomena during solidification of MMNCs.

In general, it is considered that whether particles are pushed or engulfed during solidification depends on the velocity of the particle relative to the solidification front. There are several previous models to describe such particle pushing/engulfment phenomena [8-14]; however, the past models only predict the behavior in the coarse (>> 1 μm) and fine particle (~ 1 μm) systems, and they do not accurately describe the ultrafine particle (<< 1 μm) system, presumably because the models rely on continuum mechanics. In the case of ultrafine particles these prior models do not take into consideration the random particle movements associated with Brownian motion. This random motion of ultrafine particles is imparted by unbalanced collisions of liquid atoms or molecules, and for sufficiently small particles Brownian Motion can partially or completely counteract forces such as gravity, viscous drag and thermal/concentration gradients, thus leading to engulfment rather than pushing. Therefore, the goal of the present study is to describe the impact of such random motion of particles (if any) and to develop an analytical model that can describe particle behavior. This description will be useful in predicting NP engulfment phenomena for MMNCs synthesized through solidification processing. In this document, we will consider the gravitational settling of particles with different sizes in liquid suspensions and develop a model that describes the Brownian motion-affected particle motion and then employ this as a first approximation to the case of solidification front/NP interactions to see the effect of Brownian motion on pushing/engulfment behavior in MMNCs.

Model

General approach including size considerations

As mentioned in the "introduction" section, we first consider the particle pushing and engulfment of colloidal suspension systems. The study of particle/solidification front interactions is of particular interest in the solidification of colloidal suspensions to form particle agglomerate templates, and it can be applied to the solidification front of MMCs/MMNCs. The method generally used to determine the critical velocity (v_c) for particle engulfment is to examine the force or forces that result from the solidification front (which typically push the particle away from the front) and the force or forces that oppose this pushing. From review of the previous models for MMCs [8-14], it is clear that most models use drag as the sole force that opposes the solidification front. Where drag is an actual force that counteracts the pushing force, Brownian motion is simply an imposed change of velocity in a random direction; sometimes, the movement is in the direction of the applied force enhancing the effectiveness of that force, and at other times, the movement is opposite the applied force diminishing the effectiveness of that force. However, because random motion is not a force itself, it cannot be added directly into the force balance. Incorporating the effects of Brownian motion into the force balance requires consideration of the following three physical situations.

- Large particles: if particles suspended in a liquid are large, the effects of Brownian motion are negligible and any force that acts upon the particle, be it gravity or the force of the solidification front, results in movement of the particle in the direction of the net applied force. Although drag acts to oppose this imposed motion, the drag cannot completely stop the particle from moving in the presence of an applied force. The equilibrium velocity of the system in this case is the velocity of the solidification front.
- Ultrafine particles: the behavior is much different for very small particles, as Brownian motion is a completely random resulting from unbalanced collisions between the particle and the atoms or molecules that comprise the liquid. In the case of completely random motion and no concentration gradient of particles, a passing solidification front has no effect on the particle and the particle can be engulfed. Complete Brownian motion can nullify the force of the solidification front, as well as all other forces.
- Intermediate-sized particles: it logically follows that, if large particles move in the direction of the applied force and very small particles do not move in the direction of the applied force because they move randomly, then intermediate-sized particles should likely show a mixed behavior. In this regime, particle velocity completely obeys neither Brownian motion nor the motion predicted by the force balance between the force of the solidification front and drag as described by Stokes' Law.

In the next section, the case of gravitational settling is used to determine the simplest size-dependent motion-retarding behavior that results from Brownian motion, since gravitational settling depends only on particle size, the solid and liquid densities, and gravitational acceleration.

Settling of a particle including the Brownian motion

To develop a model describing the dynamics of a particle suspended in a liquid and subjected to gravitation, we can start from a 1-D approach, where the particle is moving with a certain velocity in the direction of gravity. The settling behavior of such a particle in a liquid is governed by the balance of the forces acting upon the particle; namely, the drag force (F_d) and the gravitational or buoyant force (F_g) as shown in Fig. 1. Fig. 1 also shows an analogous situation in the case of the steady-state pushing of a particle by the solidification front. If the effect of Brownian motion is to retard motion, it can be treated, as a first approximation, as an enhancement to the drag force and applied in both instances provided a generalized behavior can be found. For gravitational settling the opposing forces are described in Eqs. (1) and (2) and the force balance (F_p) is given in Eq. (3) for particles wetted by the liquid.

$$F_d = -6\pi\mu R v \quad (1)$$

$$F_g = -\frac{4}{3}\pi R^3 \left(\rho_p - \rho_f\right) g \quad (2)$$

$$F_p = F_d + F_g \quad (3)$$

where μ, R, ρ_p, ρ_f, and g represent the viscosity of liquid, radius of dispersed particle, density of particle, density of fluid, and gravitational acceleration, respectively. To describe the motion of a particle over time, we make use of a short duration "impulse" (i.e. the product of the average force and the time interval, Δt, over which the force acts or the product of the mass of the body and its change in velocity). The impulse is a result of the imbalanced collisions of fluid molecules or atoms striking the particle under consideration. This impulse will influence the change in the Stokesian velocity, Δv_s, of the particle as settling is described by Eq. (4). Here, we approximate the particle as a perfect sphere, where m_p is the mass of the particle and can be determined from the particle volume and density.

$$\Delta v_S = \frac{F_d + F_g}{m_p} \Delta t \quad (4)$$

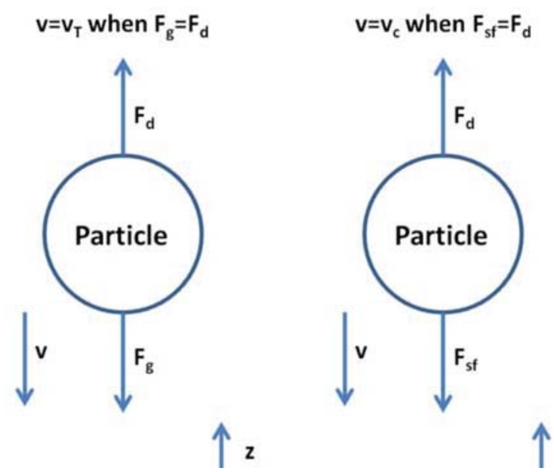

Figure 1. Schematic diagram of forces acting on a particle in a liquid in (left) gravitational settling and (right) particle pushing near solidification front.

The model is intended to identify motion induced solely by interactions between the reinforcement particle and the fluid particles and as such, a velocity equal to the terminal velocity (v_T) was chosen as the initial velocity of particle. v_T at macroscopic scales is useful in this regard as it is constant, can be determined analytically, and produces a change in position which is directly proportional to elapsed time, thus forming a straight line in any plot of distance travelled with time. v_T for any particle obeying Stokes' Law is derived by setting the magnitude of the drag force and gravitational force equal as expressed in Eq. (5).

$$F_d + F_g = -6\pi\mu R v_T - \frac{4}{3}\pi R^3 \left(\rho_p - \rho_f\right) g \quad (5)$$

$$v_T = -\frac{2}{9}\frac{(\rho_p - \rho_f)}{\mu} g R^2 \quad (6)$$

In applying the general expression for the velocity of Stokesian particle at a specific time, an iterative loop based on the impulse can be used to calculate the velocity of a particle obeying Stokes' law at a given time (v_S^t) relying on the velocity of the particle in the previous iteration ($v_S^{t-\Delta t}$) and the change in velocity during that iteration ($\Delta v_S^{\Delta t}$). When the terminal velocity, v_T, is set as the initial velocity, the cumulative distance travelled (d_S^t) for a Stokesian particle is derived to Eq. (7), where $d_S^{t-\Delta t}$ is the distance travelled by the time of t-Δt.

$$d_S^t = d_S^{t-\Delta t} + \Delta d_S^{\Delta t} = d_S^{t-\Delta t} + \left(v_S^{t-\Delta t} + \frac{\Delta v_S^{\Delta t}}{2} \right) \Delta t \quad (7)$$

Now, the effects of Brownian motion must be taken into account in addition to Eq. (7) as we have only considered the Stokesian behavior. When the elastic collisions between fluid particles (i.e., single molecule or atom) is considered, the change in velocity of particle (Δv_p) of the solid particle for the instantaneous time period of Δt due to the random motion can be given by Eq. (8) [15].

$$\Delta v_p = \frac{m_{fp} v_{fp}}{m_p} \quad (8)$$

where m_{fp} and v_{fp} are the mass and velocity of the fluid particle, respectively. To apply this equation to a 3-D case, a random angle of collision, θ, could be selected for each iteration, and it should be projected on the axis of interest as given in Eq. (9).

$$\Delta v_B = \frac{m_{fp} v_{fp}}{m_p} \cos\theta \quad (9)$$

In analog to Eq. (7) that describes the travel distance for a pure Stokesian particle, the cumulative distance travelled for a particle incorporating both the Stokesian and Brownian motions (d_{S+B}^t) may be described by the following Eq. (10) because there still is a Stokesian change in velocity due to gravity ($\Delta v_S^{\Delta t}$), and the instantaneous particle velocity and viscous friction act along the same axis as the resolved Brownian velocity ($\Delta v_B^{\Delta t}$), and these changes in velocity are additive. Note that the Brownian motion component in Eq. (10) can be obtained by Eq. (9).

$$d_{S+B}^t = d_{S+B}^{t-\Delta t} + \left(v_{S+B}^{t-\Delta t} + \frac{\Delta v_S^{\Delta t} + \Delta v_B^{\Delta t}}{2} \right) \Delta t \quad (10)$$

Application of Model and Discussion

<u>Application to the liquid composites</u>

To test the possible transitions from Stokesian to Brownian behaviors in the settling of particles, a series of simulations were performed using various particle sizes (R) in a typical liquid composite system. In Table 1, the values of the parameters used in the model which are estimates based on SiO_2 particles in H_2O are listed [16]. It should be noted that the parameters of the fluid particle are those of a water molecule, and it is assumed that the fluid particle velocity of the water molecule (v_{fp}) corresponds to its thermal velocity ($v_{th} = \sqrt{2k_B T / m_{fp}}$, where k_B, T, and m_{fp} represent the Boltzmann constant, absolute temperature, and the mass of fluid particle, respectively). In keeping with the very high velocity, the instantaneous time step (Δt) was selected as accordingly small.

μ (N s/m^2)	0.00089
ρ_p (kg/m^3)	2600
ρ_f (kg/m^3)	1000
g (m/s^2)	9.8
m_p (kg)	varies
m_{fp} (kg)	3.00×10^{-26}
v_{fp} (m/s)	523.6
Δt (s)	2×10^{-11}
v_o (m/s)	varies
R (nm)	100; 200; 400; 500; 600; 800; 1000; 10000
θ (°)	0-180 (random)

Table 1. Values of parameters used in the simulations at standard temperature and pressure [16].

To determine the general behavior of the system, 20 simulations comprised of 30,000 iterations were run for each particle size using the terminal velocity as the starting velocity for both the Stokesian and (Stokesian + Brownian) models using Eq. (7) and Eq. (10), respectively. Particle position was tracked for each iteration to calculate differences in distance travelled with time. Examples of the distance travelled for each case are illustrated in Fig. 2. Because of the stochastic nature of the system, there can be some variations between simulations. For this reason, average distances were used in determining the general behavior of the system and show that for large particles, the motion is described by Stokes' law and the Brownian motion is negligible as expected (the dotted and solid lines in Fig. 2 nearly coincide for R=10,000 nm). As the particle size decreases, however, the Brownian motion can become more significant until the motion of the particle becomes essentially random. When the particle size is reduced to R=100 nm, it is clearly seen that the random motion becomes dominant and the particle will at some point return to its original height (i.e. move zero distance). As a result of the simulations, it was found that the velocity transitioned from the terminal velocity of the Stokesian velocity to zero velocity over a range of particle sizes. The ratio of average velocity of the particle adjusted for Brownian motion to terminal velocity could be described by $\bar{v}_{S+B} / v_T = 1/\left[1+\exp\left((R^* - R)/A\right)\right]$, where R^* is the radius at which the Brownian motion adjusted velocity of the particle is half the Stokesian velocity and A is the characteristic unit that determines the width of transition region.

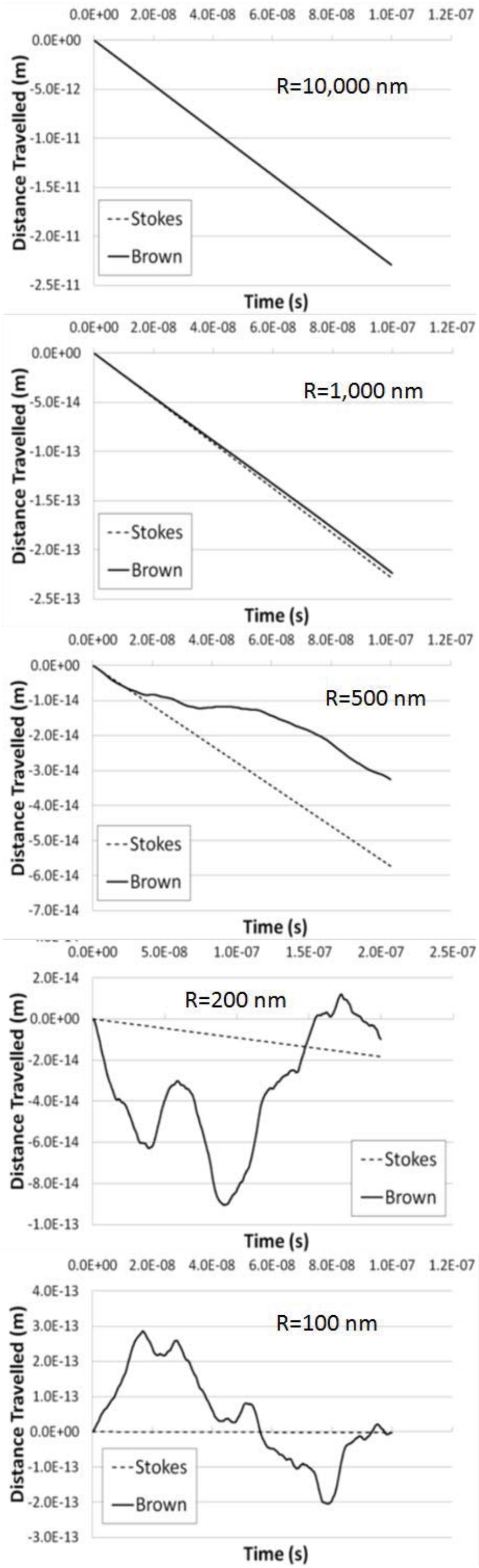

Figure 2. Model results for Stokesian settlement and Brownian motion compensated settlement of particles of various sizes (*R*).

<u>Application to the solidification front</u>

Though the analyses of the previous section are strictly applicable to gravitational settlement of particles in a liquid, they can be applied as a first approximation to particle pushing models by assuming that the change to particle velocity due to Brownian motion is generally applicable and adjusting forces as necessary. Using the right-hand side schematic of Fig. 1, we show an analogous force balance governs the behavior of steady-state particle pushing by the solidification front. In both gravitational settling and particle pushing, the particle reaches a maximum velocity when the force acting on the particle is exactly counteracted by the drag force. In the case of gravitational settling, the maximum velocity achievable by the particle is referred to as the terminal velocity, v_T, whereas in particle pushing models, the maximum velocity achieved by the particle is referred to as the critical velocity, v_c. However, the difference is only one of terminology, and given the exact similarity of the situations, terminal velocity and critical velocity may be used interchangeably. To apply the Brownian motion effect found in gravitational settling to the case of particle interactions with the solidification front, we must make use of the simplifying assumption that the same size-dependent velocity profile is also applicable in the case of particle pushing by the solidification front. While not entirely realistic, it is useful as a first approximation and v_c from any micron scale model [8-14] may be substituted for v_T as a means approximating the influence of Brownian motion on particle capture/pushing behavior.

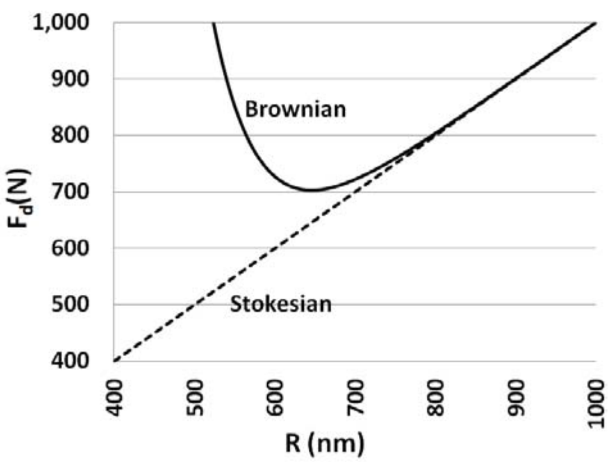

Figure 3. Drag force with variation in particle size for Stokes' law and adjusted for Brownian motion.

It is also necessary to adjust drag for Brownian motion. At small scales, where random motion dominates the behavior of the particle, any force on the particle is overwhelmed by unbalanced collisions of the atoms or molecules that constitute the fluid. However, force still acts on the particle, and the Brownian motion-type interaction of the solid and liquid particles must counterbalance this force in order to neutralize it. In this sense the particle can be thought of as being "pinned" in its location by a Brownian "force", and we propose that $F_{dB}/F_d = v_T/v_{S+B}$ and that the drag force adjusted for Brownian motion will follow the behavior shown in Fig. 3.

From this reasoning, the critical velocity (v_c) for particle engulfment can be determined from the force balance (drag force adjusted for Brownian motion = force exerted by the solidification front, $F_{dB} = F_{SF}$). Because F_{SF} is generally proportional to the inverse of the particle radius raised to some power (i.e. $F_{SF} = CR^{-x}$), we arrive at Eq. (11) that describes the general case.

$$F_{dB} = 6\pi\mu R v_c \left(1+\exp\left(\frac{R^*-R}{A}\right)\right) = F_{SF} = CR^{-x} \quad (11)$$

Solving Eq. (11) for v_c allows for the determination of the critical velocity as a function of particle size as shown in Eq. (12).

$$v_c = \frac{CR^{-(X+1)}}{6\pi\mu\left(1+\exp\left(\frac{R^*-R}{A}\right)\right)} \quad (12)$$

When Eqs. (11) and (12) are applied to the previous models [8-14] to predict the particle pushing/engulfment during solidification process, there are three theories (Chernov et al. [10], Stefanescu et al. [12], and Shanguan et al. [13]) that result in nonsensical behavior because the width of the transition, A, is infinitely large and the ratio of critical to terminal velocities is constant (i.e., 1/2) for any particle size. These models have the common feature that the force exerted by the solidification front, F_{SF} is independent of particle size, a feature that seems to be inconsistent with experimental evidence. In the case of a model such as that of Uhlman et al. [9], in which F_{SF} is inversely proportional to the particle size, the following Eq. (13) can be derived to clearly define the ratio of critical engulfment velocity at a given radius to the critical engulfment velocity at the critical radius. It is then possible to create a map to show the Stokesian and Brownian behaviors depending on the velocity ratio and R/R^*. In Fig. 4, we clearly show that there are three different particle pushing regimes for the assumed solidification front velocity ($v_c(R)/v_c(R^*)$=0.7).

$$\frac{v_c(R)}{v_c(R^*)} = \frac{2}{\left(\frac{R^2}{R^{*2}}\right)\left(1+\exp\left[\frac{R^*}{A}\left(1-\frac{R}{R^*}\right)\right]\right)} \quad (13)$$

When particles are small (left-hand side regime in Fig. 4), therefore, Brownian motion effects can cause the engulfment of the particle, which may result in an activation of Orowan strengthening mechanism. For intermediate sized particles (middle regime in Fig. 4), the reinforcement particles are expected to be pushed and grain refinement by growth restriction should occur where the strength improvement is due to grain size refinements as described by the Hall-Petch relation. Large particles (right-hand side regime in Fig. 4) are again engulfed and strengthening would be due to the large difference in coefficient of thermal expansion (CTE) between the reinforcement and the matrix, causing geometrically necessary dislocations (GND) at the interface and thus increasing strength. It must be noted that the map shown in Fig. 4 is based on the empirical fitting parameters using an assumed solidification front velocity, but it is thought that the current work elucidate how the Brownian motion effect is incorporated to understand the activation of strengthening mechanism, and the model is qualitatively consistent with the experimental data available from the solidification experiments of colloidal suspensions and MMNCs.

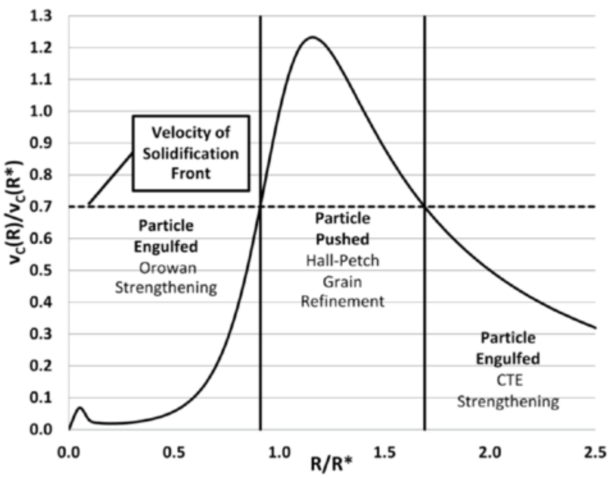

Figure 4. Representation of particle pushing/engulfment and the corresponding strengthening mechanisms as a function of particle size and critical particle size ratio.

Conclusion

In the present work, the authors have developed a theoretical model to describe the influence of particle size on settling behavior in liquids that includes the influence of Brownian motion, which is significant in the case of ultrafine particles. The model demonstrates that as the particle size decreases the deterministic Stokes' Law settling behavior breaks down. The effects of Brownian motion become more significant and eventually, at a critical particle size, become the dominant factor governing particle motion. By applying the developed model, we predict that the size of the particle will influence whether it is pushed or engulfed during solidification of the liquid, and, in the case of MMCs or MMNCs, breaks the strengthening mechanisms into three regimes. Very large particles and agglomerates will be engulfed and will strengthen the material through a mechanism whereby geometrically necessary dislocations are caused by the differences in coefficients of thermal expansion (CTE) between the matrix and the reinforcement. As the particle size decreases, intermediate-sized particles or agglomerates of NPs can be pushed and grain refinement can occur by grain growth restriction leading to mainly Hall-Petch strengthening. With continued decrease in particle size, the model predicts a reversal of behavior, where Brownian motion effects cause particle engulfment and the strengthening effects will be mainly described by the Orowan mechanism.

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Government purposes notwithstanding any copyright notation herein.

Nomenclature

A = characteristic unit (determines width of transition region)
d_B = cumulative distance travelled for a particle adjusting for Brownian Motion
d_S = cumulative distance travelled for a particle obeying Stokes' Law
Δd_S = distance travelled by particle in a single iteration for a particle obeying Stokes' Law
F_d = viscous drag force on a particle
F_{d_B} = Drag adjusted for Brownian motion
F_g = gravitational force on a particle
F_p = resultant force on a particle
F_{SF} = force exerted by the solidification front
g = gravitational acceleration
I = impulse
k_B = Boltzmann constant
m_{fp} = mass of fluid particle
m_p = mass of particle
R = radius of particle
R^* = critical radius of a particle at which Stokesian and Brownian velocity are equivalent
Δt = time step
v = velocity of particle
$\bar{v}$ = average velocity
Δv_B = change in velocity of particle adjusting for Brownian Motion
v_c = critical velocity for engulfment
v_{fp} = velocity of fluid particle
Δv_p = change in velocity of the particle due to the Brownian motion
Δv_S = change in velocity of particle obeying Stokes' Law
v_T = terminal velocity of particle
$v_{(t)}$ = velocity of particle at time (t)
v_{th} = thermal velocity
θ = angle of fluid particle velocity as measured from the direction in which gravity is acting
μ = viscosity of liquid
ρ_f = density of fluid
ρ_p = density of particle

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