The synergy of modeling and novel experiments for melt crystal growth research

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Abstract. Computational modeling and novel experiments, when performed together, can enable the identification of new, fundamental mechanisms important for the growth of bulk crystals from the melt. In this paper, we present a compelling example of this synergy via the discovery of previously unascertained physical mechanisms that govern the engulfment of silicon carbide particles during the growth of crystalline silicon.

1. Introduction

The engulfment of foreign particles during the growth of multicrystalline silicon is a problem during the production of high-quality, low-cost photovoltaic devices. In particular, carbon contamination of the melt, from the original silicon feed and via gas phase reaction and transport from hot furnace internals, leads to the formation of silicon carbide (SiC) particles which may be engulfed during crystal growth and adversely affect the subsequent processing of solar cells [1].

These issues have motivated experimental analyses of particle incorporation during the directional solidification of silicon ingots [2, 3]. A common conclusion of these studies was that classical theories for engulfment were unable to describe the behavior of SiC engulfment. Since melt convection significantly affects engulfment, microgravity experiments have been performed in conjunction with terrestrial studies [4,5]. These experiments have provided the best data yet available for SiC-Si engulfment; however, accompanying theoretical analyses were still unable to provide a real quantitative correlation with the experimental results [4,6].

In the following discussion, we show rigorous numerical computations that provide a quantitative representation of the experimental results for this system via a predicted scaling of critical engulfment velocity with particle radius of $v_c \sim R^{-5/3}$. Prior, classical engulfment theories predict either $v_c \sim R^{-1}$ or $v_c \sim R^{-4/3}$. Informed by our computational results, we further describe a simple analysis that explains these scalings.

2. Experiments

Figure 1 illustrates the ParSiWal (Partikeleinfang bei der Siliziumkristallisation im Weltall) project, which was designed to study the engulfment of SiC particles during the solidification of silicon [4,5]. The experiments were conducted via the seeding of a silicon rod with pre-synthesized SiC particles (Figure 1a), which was then placed in a mirror furnace (Figure 1b) and flown in a low-orbit sounding rocket (Figure 1c) to achieve solidification and engulfment under microgravity conditions. The same growth system was also employed on earth for additional studies.
Figure 1. Microgravity and terrestrial experiments measure critical conditions for SiC particle engulfment during silicon growth [4,5]. Right: Silicon sample, seeded with SiC particles, in crucible. Middle: ELLI mirror furnace in which growth is conducted. Right: TEXUS 51 rocket flight to achieve microgravity experimental conditions.

Figure 2. (a) A schematic depiction of particle engulfment during solidification. (b) A computation of a SiC particle article being engulfed by a silicon solidification front by our numerical model. Geometry and temperature isotherms are shown on the left, with the corresponding finite element mesh shown on the right.

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3. Model and experimental results
We have developed a rigorous numerical model for engulfment that is free from most of the simplifying assumptions that have been employed in previous approaches [7] and have reported steady-state and dynamic studies of engulfment during crystal growth in [8–10].

Our model describes a solid particle interacting with a solidification front, as depicted in Figure 2(a), with a typical example of a computation of a SiC particle by silicon shown in Figure 2(b). The crystal solidifies upward with a growth rate $v_g$, and, as melt-solid interface approaches the particle, repulsive van der Waals forces push it away from the interface, imparting a particle velocity $v_p$. Due to the upward particle motion, liquid must flow into the gap to fill the volume previously occupied by the particle, which results in hydrodynamic drag. If the drag forces—which hinder the particle from moving together with the advancing solid-liquid interface—dominate, the particle will be engulfed into crystal. Thus, a force balance on the particle is the pivotal step in modeling its engulfment. We will return to this force balance to explain the predicted scalings, by different models, of critical engulfment velocity with respect to particle size.

The experimental data and the results of a series of computations of engulfment are presented in Figure 3, which shows growth velocity versus particle diameter in a log–log plot. The terrestrial experimental conditions resulting in engulfed particles are represented by the solid, red squares, whereas pushed particles (not engulfed) are shown as open, green circles. The
Figure 3. Experimental data and engulfment models for the SiC-Si system [10]. The symbols denote data from terrestrial experiments; the star denotes a high-confidence engulfment observation from a microgravity experiment. Curves show predictions of the critical velocity and mark the boundary between particle pushing (to the left and below) and engulfment (to the right and above). The black curves represent prior, classical models for engulfment. The results from our finite-element model (FEM) are shown by the blue, solid curve and the pink, dotted curve. The position and slope of the curves are discussed in the text.

The curves in Figure 3 indicate various model predictions for the critical velocity of engulfment, $v_c$, as functions of particle size. All have been calibrated to intersect the microgravity datum (star) to account for the unknown value of the Hamaker constant for this system, which sets the magnitude of the van der Waals repulsive force. These critical velocity curves should therefore separate the data points representing engulfed and pushed particles.

The two black lines show predictions for all prior, classical models of engulfment. The dashed, black line exhibits a slope of -1 and represents models that predict a scaling of critical velocity, as $v_c \sim R^{-1}$, such as those described in [2,11,12]. The solid, black line represents models that have more rigorously included Gibbs-Thomson curvature effects and pre-melting on the solidification interface [13,14] and predict a straight line with a slope of -4/3, thereby giving rise to a scaling of $v_c \sim R^{-4/3}$. Significantly, these classical models are not able to quantitatively represent the experimental data for this system; namely, the curves do not divide the data points representing engulfed and pushed states.

In contrast, our finite-element numerical model, shown in Figure 3 by the solid, blue curve (for microgravity) and the dotted, pink curve (including terrestrial gravitational effects), is able to quantitatively correlate these data. Namely, all of data points of the engulfed states lie above these curves, while pushed states (particles not engulfed) lie below them. Such agreement between theory and experiment has heretofore been unattainable for this silicon carbide–silicon system.

The success of our numerical model in describing these data is due to its steeper slope,
measured as approximately $-1.675$, from which we deduce a scaling of $v_c \sim R^{-5/3}$. Significantly, this scaling has not, to our knowledge, been observed nor predicted in prior studies of engulfment. While we have addressed the origin of this scaling in some detail in a prior work [10], we present some simpler arguments below.

4. Analytical scaling arguments

Under critical engulfment conditions, the pushing force on the particle arising from van der Waals effects is just balanced by drag forces. We approximate these as:

$$\frac{2AR^3}{3d_{min}^2(2R+d_{min})^2} = \frac{6\pi \mu R^2 v_c}{d_{min}},$$

where the left-hand side represents Hamaker’s solution [15] for the van der Waals force and the right-hand side is the drag computed by lubrication theory [16], both derived for a sphere approaching a planar interface. Here, we represent the particle radius by $R$, the minimum gap thickness by $d_{min}$, and the critical solidification and particle velocity as $v_g = v_p = v_c$ (see Figure 2); $A$ is the Hamaker constant, and $\mu$ is the melt viscosity.

If we consider that the particle radius is much greater than the minimum gap thickness, $R \gg d_{min}$, then the above expression can be simplified and rearranged to show the dominant scaling behavior:

$$R d_{min}^2 \sim R^2 v_c d_{min},$$

$$\Rightarrow v_c \sim (R d_{min})^{-1}.$$

The simplest classical theories for engulfment [2, 11, 12] assume that the gap between the particle and solidification interface is determined solely by molecular interactions, in which case $d_{min}$ is independent of the particle radius, giving, via Eq. (3), a scaling of $v_c \sim R^{-1}$. More rigorous classical models that included Gibbs-Thomson curvature and pre-melting on the solidification interface [13, 14] predict that $d_{min} \sim R^{1/3}$. With this result, Eq. (3) predicts $v_c \sim R^{-4/3}$.

Our computations for the SiC-Si system [10] showed a significant, previously unappreciated interaction between particle-induced deflection of the solidification interface, via the effects of heat channeling through the particle when its thermal conductivity is greater than that of the melt, and a flattening of the most curved portion of the interface, via the Gibbs-Thomson effect. Thus, for a range of particle sizes between approximately 10–100 $\mu m$ in this system, the solidification interface takes on a rather complicated shape. We argue that this complicated interface shape has different effects on the van der Waals repulsion and hydrodynamic drag, leading to a reinterpretation of the force balance of Eq. (2) as:

$$\frac{R}{d_{edW}^2} \sim \frac{R^2 v_c}{d_D},$$

$$\Rightarrow v_c \sim \frac{d_D}{R d_{edW}^2},$$

where we have introduced different gap thicknesses $d_{edW}$ and $d_D$ for computation of the van der Waals and drag forces, respectively.

We argue that the short-range nature of the van der Waals force makes it most sensitive to the minimum approach distance, so that $d_{edW} \approx d_{min}$ and, following prior scaling arguments [13,14], $d_{edW} \sim R^{1/3}$. However, the net hydrodynamic drag is computed via an integration along the
The size of this gap varies, made larger in general by the heat flow through the particle but decreased in thickness at the centerline, where the Gibbs-Thomson effect flattens the deepest, most curved portion of the interface; see [10] for more details. We posit that the outcome is a drag force that does not significantly change with gap, so that $d_D$ can be considered to be constant with respect to $R$. Use these scalings for $d_{vdW}$ and $d_D$ in Eq. (5) leads to the observed behavior of $v_c \sim R^{-5/3}$.

5. Conclusions
Motivated by the inability of classical models to describe experimental data on the engulfment of SiC during silicon crystal growth, we have developed a rigorous, numerical model to study this system. For the first time in over a decade of research on SiC inclusions in silicon, our model is able to provide a quantitative correlation of experimental results, and we are able to unequivocally identify the underlying physical interactions that give rise to the observed behavior. In particular, we identified a significant and previously unascertained interaction between particle-induced interface deflection, originating from the thermal conductivity of the SiC particle being larger than that of the surrounding silicon liquid, and curvature-induced changes in melting temperature arising from the Gibbs-Thomson effect. The interface shapes arising from these interactions produce different effects on the van der Waals and hydrodynamic drag forces and result in a scaling of $v_c \sim R^{-5/3}$ for particle sizes of relevance in this system. This synergy of modeling and experiments has thus provided new insight into the fundamentals of crystal growth.

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