**Computer Simulations of the Aluminium–Silicon Anomalous Eutectic Growth Based on Multiphase Field Method**

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Aluminium–silicon anomalous eutectic growth has been studied numerically using a phase-field model developed to predict multiple phases. The Si phase grew very slowly in a melt of eutectic composition, but then grew substantially faster when in contact with the solidifying Al phase. The Al-liquid interface was irregular while the Si-liquid interface was flat as a consequence of the low interfacial energy between phases. The Si phase grew very slowly in a melt of eutectic composition, but then grew substantially faster when in contact with the solidifying Al. It also has been shown that the melt is more likely to be trapped within the Si phase than in the Al phase.

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1. Introduction

Eutectic alloys are classified as normal and anomalous. In normal structures, the two phases appear either as alternate lamellae or as rods. A theoretical description of normal eutectic growth was proposed some years ago by Jackson and Hunt. Anomalous structures occur in systems when one of the solid phases has a high entropy of melting, and a variety of microstructures such as broken lamellar, flake, fibrous and complex regular then are formed on solidification. One of the most commercially important of these is the flake structure of silicon in aluminium–silicon alloys. The nucleation and growth of the aluminium–silicon eutectic has been studied extensively experimentally, but understanding of microstructural evolution is not fully established.

Phase-field modelling has recently emerged as a powerful computational approach to study microstructural evolution in metal and alloys. Simulations of normal eutectic growth by means of phase-field modelling have been reported in a number of papers, and regular eutectic morphologies have been reproduced successfully. However, the simulation of anomalous eutectic growth has not been reported.

The aim of the present paper is to present a study of aluminium–silicon anomalous eutectic growth by means of numerical simulations. In order to describe the solidification behaviour, a mathematical nucleation criterion has been introduced in the phase field model. The predicted growth morphologies have been compared with experimental observations.

2. Model description and simulation procedure

2.1 Multiphase-field model

Aluminium–silicon eutectic structures form when the system temperature falls below 577°C. For equilibrium solidification, the solute concentration in the eutectic melt is initially about 12.2 mol% silicon. Two solid phases, Al (fcc crystallographic structure) and Si (diamond structure), then nucleate and grow at this stage. Following the approach of Tiaden et al., two phase-field order parameters $\phi_1$ and $\phi_2$ can be introduced to indicate the physical state of the system, such that

$$\phi_0 = 1 - \phi_1 - \phi_2$$

where $\phi_1 = 1$ represents the solid Al phase, $\phi_2 = 1$ the solid Si phase, $\phi_1 = 0$ and $\phi_2 = 0$ the melt, $0 < \phi_1 < 1$ and $\phi_2 = 0$ the interface between solid Al and liquid, $0 < \phi_2 < 1$ and $\phi_1 = 0$ the interface between solid Si and liquid, and $0 < \phi_1 < 1$ and $0 < \phi_2 < 1$ the interface between solid Al and Si. Neglecting any phase transition between the solid Al and Si, the interface between Al and Si is formed by from the liquid to solid transformation:

$$\text{Liquid} \rightarrow \text{Al} + \text{Si}$$

Neglecting any contribution from any tri-junctions between Al, silicon and liquid (i.e. where $\phi_1 > 0$, $\phi_2 > 0$ and $\phi_0 > 0$) to the free energy of the system by assuming that the two-phase solid region dominates the phase transitions, one defines

$$h(\phi_i) = \phi_i^4(6\phi_i^2 - 15\phi_i + 10)$$

where $i = 0, 1$ or 2. The term $h(\phi_i)$ effectively defines the volume fraction of phase $i$ (although this definition is not valid for any tri-junction region because $\sum_{i=0}^{2} h(\phi_i) \neq 1$ when $\sum_{i=0}^{2} \phi_i = 1$). The system’s Gibbs energy can be constructed using the Ginzburg-Landau theory, namely:

$$G = \int \left[ \frac{1}{2} \sum_{\alpha=0}^{2} \sum_{\beta<\alpha} \left( \frac{\gamma_{\alpha\beta}}{4} \phi_\alpha \nabla \phi_\alpha \phi_\beta \nabla \phi_\beta + \frac{1}{\delta_{\alpha\beta}} \phi_\alpha \phi_\beta \right) + \sum_{\alpha=0}^{2} h(\phi_\alpha)g_\alpha(c_{\alpha}, T) \right] dv$$

where $v$ represents the whole system volume. The term $\gamma_{\alpha\beta}$ is the gradient energy coefficient at the $\alpha$-$\beta$ interface, and can include the effect of interface anisotropy through the introduction of an orientation-dependent function:

$$\gamma_{\alpha\beta} = \gamma_{\alpha\beta} + \gamma_{\alpha\beta}^a \left[ 1 + \gamma_{\alpha\beta} \cos(k_{\alpha\beta} \theta_{\alpha\beta}) \right]$$
where $\tilde{e}_{\alpha\beta}$ is the gradient energy coefficient for a planar interface and can be determined from $\tilde{e}_{\alpha\beta} = \sqrt{3}\lambda_{\alpha\beta}\sigma_{\alpha\beta}/1.1^{13}$, $\lambda_{\alpha\beta}$ is the $\alpha-\beta$ interface thickness, $\sigma_{\alpha\beta}$ is the interfacial energy, $\gamma_{\alpha\beta}$ and $k_{\alpha\beta}$ are constants. The term $\theta_{\alpha\beta}$ represents the interface orientation and obeys the relationship $\cos \theta_{\alpha\beta} = \tilde{e}$.

2.2 Nucleation criterion

The relationship $\cos \theta_{\alpha\beta} = \tilde{e}$ gives the relationship between interface orientation and interfacial energy.

In equation (3), $\omega_{\alpha\beta}$ is the excess interfacial energy coefficient and is satisfied by $\omega_{\alpha\beta} = \lambda_{\alpha\beta}/(26.4\sigma_{\alpha\beta}).^{13}$ $g_a$ is the free energy density of the bulk $\alpha$ phase, and $c_a$ is the solute concentration of the $\alpha$ phase. Assume that the solute concentrations in the solid Al ($c_1$) and Si ($c_2$) phases depend on local the temperature only and the values are those defined by the solidus in equilibrium phase diagram, one has the following governing equations:

\[
\left( \frac{\partial \theta_{\alpha\beta}}{\partial t} \right)_{c,T} = -M_{c,T} \left[ \frac{\partial \eta_{\alpha\beta}}{\partial T} \right]_{c} + \frac{\partial \eta_{\alpha\beta}}{\partial \theta_{\alpha\beta}} \frac{\partial \theta_{\alpha\beta}}{\partial T} + \eta_{\alpha\beta} \frac{\partial^2 \eta_{\alpha\beta}}{\partial \theta_{\alpha\beta}^2} \left( \frac{\partial \theta_{\alpha\beta}}{\partial T} \right)_{c,T} \]

\[
\left( \frac{\partial C_a}{\partial t} \right)_{c,T} = \frac{\gamma_a}{V_a} (\phi_a) \nabla \cdot (D_a \nabla C_a) \]

\[
\left( \frac{\partial T}{\partial t} \right)_{c,T} = \nabla (K_T \nabla T)_{c,T} \]

where $\phi = [\phi_1, \phi_2]$ and $c$ is the total solute concentration and is given by:

\[
c = \sum_{a=0}^{2} h(\phi_a) c_a \]

$M_{c,T}$ is the phase-field mobility for liquid-$\alpha$ phase transition, and is determined by the interface kinetics.\(^{15}\) The term $\gamma_a$ in eq. (5) is the phase-field driving force for the liquid-$\alpha$ phase transition and is given by:

\[
\gamma_a = \frac{\partial \gamma_0}{\partial c_0} (c_0 - c_a) - (g_a - g_a) \]

The terms $V^o(\phi_a)$ and $N^o(\phi_{\text{atom}}, \phi_a)$ are the effective volume and effective surface area of the $\alpha$ phase. $D_a$ is the solute diffusivity within the $\alpha$ phase. The connecting conditions in conjunction with the governing equations are:

\[
\hat{c}_0 = \sum_{a=1}^{2} \left[ c_a + [1 - h(\phi_a)]c_0/[1 - h(\phi_a + \delta \phi_a)] \right] \]

\[
\delta T = -\sum_{a=1}^{2} \left[ L_{\alpha\alpha} h(\phi_a + \delta \phi_a) - h(\phi_a)/c_{\phi,a} \right] \]

where $\hat{c}_0$ is the solute concentration of liquid when the phase field order parameters have changed from $\phi_a$ to $\phi_a + \delta \phi_a$, $c_0$ is the solute concentration before this change happens, $\delta T$ is the temperature increase arising from the change of phase field order parameter, $L_{\alpha\alpha}$ is the latent heat of fusion and $c_{\phi,a}$ is the specific heat of the solid being formed during the liquid-$\alpha$ phase transition.

2.2 Nucleation criterion

Classical nucleation theory\(^{16}\) gives the relationship between nucleation rate $I$ and the thermodynamic barrier to nucleation $W$ at a temperature $T$ as:

\[
I = A \exp \left( -\frac{W}{kT} \right) \]

where $A$ is a constant and $k$ is Boltzmann’s constant. Equation (12) means that the possibility for the formation of a nucleus increases when the thermodynamic barrier decreases.

In order to simulate nucleation in an heterogeneous system, we define a nucleation criterion:

\[
P_a = \begin{cases} 1 & \text{if } |x| \leq \Xi_{0,a}(c_{0,a}^\text{nl} - c_0) \\ 0 & \text{else} \end{cases} \]

where $x$ is a random function with a value between $-1$ and $+1$, $c_{0,a}^\text{nl}$ is the solute concentration defined by the liquidus, $\Xi_{0,a}$ is a weight factor. It can be seen from equation (13) that the possibility of nucleation is proportional to the deviation in solute concentration from the equilibrium value $c_0$, and can be controlled by the factor $\Xi_{0,a}$.

2.3 Simulation procedure

The symmetry of the interface between Al and melt is well known as $k_{10} = 4$. The symmetry of the interface between Si and liquid is not known, but experimental observations show five-fold branched silicon particles.\(^{17}\) Therefore, a value of $k_{10} = 5$ has been assumed in the present simulations. The initial melt contains 12.2 mol% silicon, which is the eutectic composition. Noise was introduced to the system via perturbations to the solute concentration using the expression:

\[
c_{0,a}^\text{nl} = c_0 \left[ 1 + \chi |x| \left( \frac{2}{1 + |x|} \right) h(\phi_a) \right] \]

where $c_{0,a}^\text{nl}$ and $c_0$ are the solute concentrations of the liquid with and without a perturbation, respectively, $\chi$ is a random function with a value between $-1$ and $+1$, and $\theta$ represents the intensity of the noise.

The system is defined as isothermal with an undercooling of 2.5 K. The parameters used for the multiphase-field are listed in Table 1. Two nucleation cases have been considered. The first is for homogeneous nucleation where a defined number of nuclei is put into the melt randomly. The second is for heterogeneous nucleation where the number of nuclei is not defined and the nuclei are introduced by means of equation (13).

A commercial thermodynamic database, MTDATA,\(^{20}\) has been integrated with the multiphase-field model so that thermodynamic quantities such as Gibbs energies of the
system and of each phase, the chemical potential of the liquid and the equilibrium composition of each phase can be calculated with convincing accuracy and reliability.

The governing equations are solved by a finite difference technique in a two-dimensional uniform grid. The mesh size was chosen as $\Delta x = 7.15 \, \text{nm}$ so that there are four grids across interfaces. The time step was calculated using the expression:

$$\Delta t = 0.1 \Delta x^2 / D_0$$  \hspace{1cm} (15)

Equation (15) ensures that the stability and accuracy of the finite difference technique are well maintained. The Neumann boundary condition was used for the solute concentration so that the total amount of the solute is maintained throughout the simulations.

3. Results and Discussions

3.1 Homogeneous nucleation

Ten Al and five Si spherical seeds or nuclei were put into the logical frame randomly at a temperature of 574.5°C. The temperature was kept constant and uniform until the completion of solidification. The evolution of the phase-field microstructure was recorded and is plotted in Fig. 1. Figure 1(a) illustrates the random distribution of the seeds. The light grey colour represents Al, dark grey for the melt and black for Si. The phase-field distribution at a time

$$t = 5 \, \text{m} \, 112 \, \text{s},$$

was chosen as $\frac{1}{15}$

$$t = 0,$$

$$t = 5.112 \, \mu s,$$

$$t = 51.12 \, \mu s,$$

$$t = 76.68 \, \mu s,$$

$$t = 102.24 \, \mu s$$

and (f) $t = 168.18 \, \mu s$.

$$M_{\text{Si}}, \frac{1}{\text{mol}} \, \text{Si}$$

$$12.387$$

and (f) $t = 168.18 \, \mu s$.

$$M_{\text{Si}}, \frac{1}{\text{mol}} \, \text{Si}$$

$$11.921$$

is illustrated in Fig. 1(b). It can be seen that the Al phase grows much faster than the Si particles, some of the growing Si particles are overtaken by the Al phase with which they are in contact. It can be seen from Fig. 1(f) that some liquid also can be trapped within the solid Si phase, and so further nucleation of another solid phase would be required in order to complete solidification. The individual Si particle is still very small in Fig. 1(f). These results show good agreement with the Al–Si phase-diagram and experimental observations.

3.2 With nucleation criterion

As has been illustrated in the previous subsection, any melt in which a single solid phase is growing needs seeds or nuclei of other solid phases in order to complete solidification. This can be achieved in two ways. One is by continuously introducing seeds based on homogeneous nucleation criteria. The second is by using a mathematical nucleation criterion derived for heterogeneously nucleation, i.e. equation (13).

In the simulations in the current work, one Si seed was put in the corner of the logical frame, as illustrated in Fig. 2(a). This seed grew very slow. The nucleation criterion, equation (13) with the values listed in Table 1, was applied from the start of the simulation. At a time of $t = 13.29 \, \mu s$, an Al seed forms, as shown in Fig. 2(b). The Al phase then grows
quickly towards the Si particle, and causes more nucleation of the Si phase, as shown in Fig. 2(c). At $t = 42.43\, \mu s$, another Al seed nucleates in the melt away from the growing solid phase and becomes another growth centre. The solidification was completed after a time $t = 63.39\, \mu s$, as can be seen in Fig. 2(f).

Two conclusions can be drawn from Figs. 2(a)–(f). Firstly, eutectic growth starts from the formation of an Al nucleus rather than from Si. Although the Si seed was the first to be introduced into the logical frame, eutectic growth started from the formation or nucleation of an Al seed in the melt away from the pre-existing Si particle. The solidification was completed after a time $t = 63.39\, \mu s$, as can be seen in Fig. 2(f).

It has been shown in Figs. 1 and 2 that modelling using heterogeneous nucleation provides an accurate description of solidification in the aluminium–silicon eutectic. This can be understood by considering the equilibrium and metastable liquidus lines on the Al–Si phase diagram shown in Fig. 3. During the growth of Si, the concentration of silicon in the melt decreases and the driving force for the formation of an Al nucleus increases due to the associated increase in local undercooling for the Al phase. The possibility for the formation of Al nuclei in the vicinity of solidified Si is greater than for their formation further into the melt due to local absorption of silicon from the melt by the growing Si and the limited extent of solute diffusion into the melt. However, as the growth of an Al particle increases, there will be a corresponding increase in the concentration of silicon in the melt around the Al phase and so the driving force for the formation of Si nuclei increases. The variation in solute concentration in the melt around the growing solid promotes the eutectic growth. Because the driving force for the nucleation of each solid phase is a monotonic increasing function of the deviation of the solute concentration away from the equilibrium liquidus concentration, the proposed nucleation criterion in equation (13) is reasonable.

It should be noted that the probability for the formation of an Al nucleus in the melt away from the solid has been found to be much larger than that for Si. This can also be understood from the phase diagram. It can be seen from Fig. 3 that the gradient of the liquidus line for the formation of Al is much smaller than that for Si. Hence, for the same solute deviation from its equilibrium value, the smaller liquidus gradient corresponds to a smaller undercooling, and the smaller undercooling means a smaller driving force for the nucleation. Given the heterogeneous solute distribution in the melt, the larger liquidus slope will mean that the solute distribution has a particular large influence on nucleation phenomena. In other words, the formation of Si is determined more from the original solute distribution, while the formation of Al is less so and is more related to solute fluctuations. Hence the possibility for the formation of a Si nucleus in the melt further into the melt and away from the growing eutectic solid is relatively rare.
Figure 4 is an optical micrograph taken from an experiment conducted under similar solidification conditions to those used in the above modelling. The morphology is very similar to the simulation illustrated in Fig. 2(f). Comparing the phase-field model predictions with experimental observations reported in the literature, the following similar characteristics are noted:

(a) eutectic growth starts by the nucleation of the Al phase;
(b) non-perfect structures are more likely to be formed in the Si phase;
(c) growth of Si flakes can be suppressed or stopped by the fast growing Al phase.

4. Conclusions

Aluminium–silicon anomalous eutectic growth has been studied numerically by means of a phase-field model developed to predict the formation of multiple phases. The simulated morphologies agree well with equivalent experimental observations.

The eutectic growth starts from the nucleation of the Al phase, and this is attributed to the gradient of its liquidus slope relative to that of the Si phase and the associated relative undercoolings of the two phases at a given temperature.

The interface between Si and the melt is straight due to the high interfacial energy, while the interface between Al and melt is rough or dendrite-like due to the small interfacial energy.

Liquid from the melt is more likely to be entrapped within the Si phase due to its lower growth rate when compared with the Al phase. The growth of the Si may be suppressed or stopped by it being overtaken by the faster growing Al phase.

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REFERENCES

20) MTDATA, Thermodynamic and Phase Equilibrium Modelling Software from the National Physical Laboratory, Teddington, United Kingdom.