

A COMBINED CELLULAR AUTOMATA AND DIFFUSION MODEL FOR THE PREDICTION OF POROSITY FORMATION DURING SOLIDIFICATION

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*All models are wrong,
but some are useful.*
-- G. F. D. Box

ABSTRACT

A model of the growth of microstructure and porosity during the solidification of aluminium alloys has been developed. This model incorporates the cellular automaton technique for the growth of the solid phase, a finite difference technique for the diffusion of gaseous and alloy solutes, and a combined technique for the growth of gas pores. The pores are allowed to take on a complex shape within the three-dimensional network of intergranular liquid. The nucleation of both grains and pores is governed by a stochastic model.

The sensitivity to model parameters such as grid and timestep size are explored, and comparisons made with analytical solutions for simple situations to determine the range of validity of this implementation of the model. The effects of variation of the assumed nucleation processes are studied and related to prior experimental observations.

The results of the model are compared to directional solidification and wedge casting experiments in aluminium-silicon alloys and direct-chill casting experiments in aluminium-magnesium alloys showing good correspondence of the trends but illustrating the areas in which further development of the model is needed, especially the inclusion of shrinkage pressure and improved dendritic growth models

The effect of pore geometry on the final pore size and amount is simulated by altering the pressure-volume relationship within the pores in a manner suggested by minimum surface energy simulations of individual pores. Including the restricted curvature of the pore/liquid interface and the resulting elevated pore pressure improves the fit for Al-Mg alloys compared with a simple spherical pore growth assumption.

By simulating a broad range of casting conditions and applying statistical methods, equations can be developed to apply the results of this model to larger castings for which the time required for exact computation would be prohibitive.

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SYMBOLS

Main Symbols

B_1	classical nucleation law pre-exponential
C	solute concentration
C_l^{eq}	equilibrium solute concentration in liquid
C_l^H	hydrogen concentration in liquid
C_i^H	initial hydrogen concentration in liquid
D	diffusion coefficient
F	geometry and wetting characteristics factor
f_s^g	fraction solid at which solid growth extends into a neighbouring cell
f_l	fraction liquid
f_s	fraction solid
G	temperature gradient
I	nucleation rate
k	solute partition coefficient
$\hat{k}$	curvature
k	Boltzmann's constant
L	length (measured or simulated)
m	liquidus slope
N	number density
n	amount (moles)
P	fraction (percent) porosity
Pe	Peclet number
p	cell nucleation probability
R	equivalent spherical pore radius (measured or simulated)
R	statistical coefficient of correlation from regression analysis
R	ideal gas law constant
r	radius
r_e	effective limiting radius for pore expansion
S	solubility
s	supersaturation
s	seconds
T	temperature
T^{ref}	reference temperature for linearised phase diagram
t	time
t_s	local solidification time
V	volume
V_c	volume of a cell in the model domain

v	velocity
v^g	growth velocity
ΔH_f	molar enthalpy change due to phase change
ΔT	alloy undercooling
Δv	change in domain volume
Π	pressure
Ξ	state of cellular automaton cell
α_g	grain growth constant
β	dimensionless growth constant
γ	surface tension of alloy
φ	derived parameter: $(1-(1-k)f_s)$
κ	permeability
λ	spacing
π	3.14159
σ	standard deviation (of Gaussian distribution)
ξ	random number

Subscripts and Superscripts

a	average
av	
atm	atmospheric
e	effective or averaged property
eq	equilibrium
G	referring to grains
g	growth
H	hydrogen
i	initial
l	referring to liquid phase
m	maximum
max	
min	minimum
n	nuclei or potential nuclei
p	referring to pores
r	rods
Si	silicon
s	referring to solid phase or solidification
th	threshold
σ	referring to a distribution spread

1. INTRODUCTION

The soundness of metal products depends upon the processes occurring during production. Defects formed during each stage of production can persist or modify the behaviour of the metal during subsequent processing steps. Therefore ensuring the soundness at each stage has always been a focus in the study of metal production. The prediction of porosity in solidifying metal castings is one way of helping to ensure the soundness of the final products.

Porosity in castings is a defect which results from the interaction of a number of processes: volume change, nucleation, growth of the solid phase, diffusion of dissolved species, and the interaction of interphase surfaces. Although some of these individual processes may be treated analytically, combining the processes into a predictive tool requires the numerical calculation power which has become available over the last few decades due to the development of digital computers.

In this Thesis, a computational model is presented which combines a number of numerical methods to model the behaviour of solidifying metal, diffusing chemical species, and growing bubbles along with stochastic simulations of empirical models for phase nucleation, to produce a predictive model for the number and size of pores resulting from gas dissolved in the metal.

In Chapter 2 a review of the relevant literature is presented, concentrating on mathematical and computational modelling of the solidification and pore growth processes. An introduction to the cellular automaton method with a brief historical review is included. Significant experimental results from the literature are presented and some of these are used in later chapters for validation of the model.

Chapter 3 presents in detail the theory including the assumptions and approximations used for the computational model used in this Thesis. The model is divided conceptually into the solidification model and the pore growth model, although in reality, and in the computer program, these processes are linked together.

In Chapter 4, the results of testing the solidification and pore growth submodels are presented and discussed. The solidification results are compared with the prior mathematical models of growth and with experimental results available in the literature, and with some experiments of other students at this College. The porosity model is applied to a pore in the absence of any solid phase and compared to the analytical solution.

In Chapter 5, the behaviour of the combined porosity and solidification model is explored, and the sensitivity to several of the physical and numerical input parameters is discussed. A factorial experimental design is applied to the model to determine the relative importance of interactions between the parameters. A microscale model of a the surface of a bubble interacting with solid is presented and discussed

In Chapters 6 and 7, the model is applied to specific experimental situations.

Chapter 6 presents the application to the Al-7 wt% Si alloy system and comparison with experimental findings. The model is then used to estimate the porosity in a wedge casting by applying the model over a range of conditions, extracting equations for the measures of porosity as functions of casting parameters by multiple regression analysis, then applying these to the results of a conventional finite-element casting simulation.

Chapter 7 presents the application to the direct-chill (DC) casting of Al-Mg alloys, in which the model is applied to the experimental conditions used in industrial experiments using a range of Mg concentrations. The effect of the interaction of the growing pore with the solid surface was found to be more important in this case, and the bubble surface model indicates a possible reason.

The conclusions of the study are presented in the final chapter followed by recommendations for further work in this area.

2. BACKGROUND

2.1. The Casting Process

Casting produces shaped items by allowing liquid material to solidify within a mould containing a cavity of the desired shape. Comprehensive textbooks covering the subject in great detail have been written by Chalmers [1], Flemings [2], Kurz and Fisher [3], and Campbell [4].

In most casting processes, it is desired to produce final objects which are homogeneous and reproducible. During the casting process some features may form within the body of the casting rendering it inhomogeneous. These features are generally known as casting defects. Such defects may include compositional inhomogeneity (macrosegregation), foreign particles (inclusions), and voids (porosity). Those defects having their origins in the solidification process are known as solidification defects. If these features cannot be entirely eliminated, it is desirable to be able to predict their location and type. This chapter will concentrate upon porosity and upon segregation and inclusions as they influence porosity.

Macroscopic segregation occurs when a casting of a multi-component material solidifies in a non-uniform fashion. The solid phase will in general have a different composition from the liquid from which it forms and hence there will be some segregation or build-up of some of the components in the liquid phase, and those areas to solidify last will have a different composition than those which solidify first. Rapid solidification, grain refinement, and uniform cooling help to ensure that these areas are finely divided and uniformly dispersed throughout the casting thus providing macroscopic homogeneity in the properties of the material throughout the casting. For castings of complex shape, it is often difficult to ensure uniform cooling; computer simulations of the heat flow within the casting and mould are now used with much success to aid in the design of castings, for example Major *et al.* [5] included such simulations in the development of a complex automotive suspension part.

Inclusions may occur by formation of insoluble reaction products such as oxides within the melt or entrainment of material eroded from the mould during pouring. The latter effect is more likely to occur when the fluid flow within the melt delivery system or the mould itself is turbulent. In such cases, the forces exerted by the fluid upon the mould material can be quite large. The occurrence of this behaviour in castings of complex shape can be predicted by numerical simulations, which are now routinely used to help modify mould and gate shapes to eliminate unwanted turbulence.

Porosity may result from three distinct sources which also interact with one another. One source of porosity is entrapped bubbles of insoluble gas which persist during solidification and remain within the final casting. These are likely to occur when the filling of the mould is highly turbulent. Another source of porosity is the development of a large negative pressure which forms due to regions within the casting solidifying after all the surrounding material has solidified, resulting in the material shrinking and rupturing. This may be exacerbated by macrosegregation, which in some cases allows pockets of liquid to exist at a much lower temperature due to the effect of composition on the solidus. A third source of porosity may be dissolved gases within the liquid metal which come out of solution and form bubbles during solidification. This process may be exacerbated by the pressure drop due to shrinkage, and by the presence of small amounts of entrapped insoluble gases.

2.2. Solidification

The process of solidification has been the focus of experimental and theoretical studies for centuries. Flemings [2] and Kurz and Fisher [3] provide good in-depth coverage of the subject primarily focussed upon metals, and Mullin [6] provides a slightly different coverage from a chemist's viewpoint, in particular addressing precipitation from aqueous solutions and the solidification of glasses and polymers. Of particular interest in the current study are the development of features on the small or microscopic scale due to the interaction of substances dissolved in the liquid with the developing solid phase. Specifically, the processes of nucleation and growth of the solid and of the gas phase will be studied.

The processes of nucleation and of growth of the solid are of primary importance to the final structure, and in the case of porosity formation, they create the boundaries and determine the chemical environment in which the pores form. During solidification, these processes compete for the formation of new solid, and in modelling they must both be considered.

2.2.1. Nucleation

Once a liquid (or other phase) is in a state in which the single phase is no longer in equilibrium – superheated, supercooled or supersaturated – a second phase may form. However, this does not invariably happen immediately; there is a barrier to this transformation, and one or more nucleation events must occur. The three possible mechanisms for nucleation which must be considered are: (i) homogeneous nucleation, (ii) heterogeneous nucleation, and (iii) growth from existing substrates such as gas pockets or

metastable particles (which is not truly a nucleation process but nonetheless occurs under certain conditions).

Homogeneous Nucleation

The classical model of homogeneous nucleation is developed by calculating a critical degree of deviation from equilibrium required for nucleation, from thermodynamic and kinetic principles. The balance of free energy due to formation of a particle of the new phase is determined. When there is a net decrease, then nucleation may occur. However, this balance depends upon the size of the new particle, since the energy required to create the surface must be considered as well as the energy released due to the transformation of the volume of the particle. The surface area increases as the second power of the linear dimension whereas the volume increases as the third power, for particles of similar shape. Thus a particle greater than a certain radius will be stable, but there is a barrier to the formation of such a particle [6].

The energy balance is formed by taking into account the decrease in free energy due to the formation of a certain volume of the new phase, and the increase due to the formation of the surface of that phase; in the simplest case the particle is assumed to be a sphere of radius r and the balance is:

$$\Delta G = \text{area term} - \text{volume term} = 4\pi r^2 \gamma - \frac{4}{3} \pi r^3 \Delta G_v \quad (2-1)$$

where γ is the specific energy of the surface between the phases and ΔG_v is the free energy change per unit volume of the new phase. In order to deduce whether the sphere will grow or shrink, we determine the derivative of ΔG and if it is negative (which corresponds to a release of energy as r increases) the sphere will grow. When $\frac{d}{dr} \Delta G$ is zero, we have the critical radius r_c above which a sphere may grow:

$$\begin{aligned} \frac{d}{dr} \Delta G &= 8\pi r \gamma - 4\pi r^2 \Delta G_v = 0; \\ r_c &= \frac{2\gamma}{\Delta G_v} \end{aligned} \quad (2-2)$$

from which the critical volume of a spherical particle may be calculated using: $V_{sph} = \frac{4\pi r_c^3}{3}$.

Nucleation Rate

The calculation then continues by applying statistical mechanics to the temperature distribution, to estimate the size of equilibrium fluctuations giving rise to clusters of atoms or

molecules of the new phase. At a certain temperature, the rate of formation of clusters which are large enough to exceed the critical radius becomes high enough to allow nucleation. This depends somewhat upon the time scale of interest; however, the formation rate as a function of temperature increases quite sharply, hence there is a relatively narrow range of temperatures in which observable nucleation rates occur. The degree of undercooling, superheat or supersaturation at which this sharp rise occurs is known as the critical undercooling, superheat or supersaturation.

This formula may be written [2] for the rate of formation of clusters of volume V :

$$I = B_1 \frac{D}{D_m} e^{\left[\frac{16\pi\gamma^3 T_m^2 V^2}{3\Delta H^2 \Delta T^2 kT} \right]} \quad (2-3)$$

where I is the nucleation rate, D is the diffusion coefficient, D_m is the diffusion coefficient at the equilibrium melting point, k is Boltzmann's constant, T_m is the melting temperature, ΔT is the undercooling, and T is the temperature. Note that the volume appears in the exponential and hence this rate is very sensitive to the volume. The pre-exponential B_1 may be taken as a constant of about 10^{33} according to Flemings who (among others) has covered this derivation in greater detail [2, 6].

Heterogeneous Nucleation

The occurrence of homogeneous nucleation is limited to very restricted situations and experimentally observing this process is somewhat involved.

Geometry

In order to form a particle of critical radius adjoining a surface of a separate phase, a cluster of smaller total volume is needed. The shape of the particle is truncated as illustrated in Figure 2-1, in which a hemispherical particle of phase B is shown adhering to a surface of phase C (heterogeneous particle). In this case the surface is assumed to be flat and the interfacial energy γ_{AC} and γ_{BC} are assumed equal. Repeating the energy balance of Equations 2-1 and 2-2 for the hemisphere yields the same r_c as the volume is half, and likewise the surface area is half. In this case the energy associated with the circle of cross-section of the particle need not be accounted for, in this specific case, as the interfacial energy of phases A and B with phase C are equal. Thus the critical volume is half that for the homogeneous case.

The geometry of the heterogeneous particle exerts a significant effect on the above energy balance. If we abandon the assumption that the surface is flat, but instead has a crevice, or re-entrant angle, the geometry of a nucleus forming in this crevice is such that the volume required for a given radius of the surface between the nucleus and the parent phase is greatly reduced. This is illustrated in Figure 2-2, in which cross-sections of conical indentations are shown. In these cases, the interfacial energy between phase *A* and phase *C* is once again assumed to be the same as that between phase *B* and phase *C*, resulting in a contact angle of 90°. In this simple case, the volume of phase *B* to form a particle of critical radius is:

$$V_{cone} = \frac{2\pi r_c^3}{3} [1 - \cos \alpha] \quad (2-4)$$

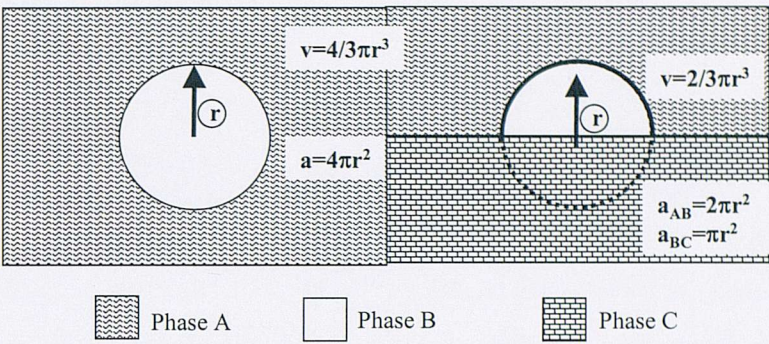


Figure 2-1. The geometry of a particle of phase B (gas) forming from phase A (liquid). (a) As a sphere in the absence of any other phase. (b) As a hemisphere on a surface of phase C (solid).

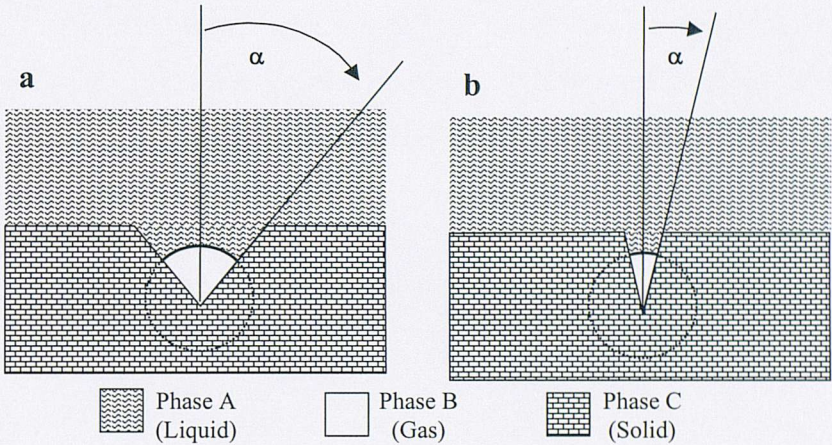


Figure 2-2. Schematic drawings of nucleation in a crevice, where (a) illustrates a cone-shaped crevice of apex half-angle $\alpha=45^\circ$ which is less sharp than (b) with an apex half-angle of 10° . For a similar contact angle at the triple junction, approximately 90° in these illustrations, much less volume is required to form a particle of the critical radius in a sharp crevice.

where α is the half-angle of the cone apex. Forming the ratio with the volume of the sphere results in the formula:

$$\frac{V_{cone}}{V_{sph}} = \frac{[1 - \cos \alpha]}{2} \tag{2-5}$$

from which a few illustrative examples may be calculated. If the angle $\alpha = 45^\circ$, the ratio is 0.14 which is a noticeable decrease, and if the angle is reduced to 10° we find that the ratio is 0.0076 which is quite a significant decrease in the required volume. If these volumes are substituted into Equation 2-3, the predicted behaviour is illustrated by the graph in Figure 2-3 where the curves for the sphere, the hemisphere the 45° cone and the 10° cone are plotted. Due to the sharp exponential nature of the function in Equation 2-3, the nucleation rate

changes from close to zero to a very large value over a narrow range of temperatures. The temperature at which this happens is the *critical temperature* for nucleation under the particular conditions assumed.

Surface energy

Abandoning the assumption that $\gamma_{AC} = \gamma_{BC}$, it may be shown that the degree of activity of heterogeneous materials as nucleation agents depends upon their surface energies with respect to both the primary phase and the nucleating phase. This effect can be very significant especially when the nucleating phase B wets the heterogeneous phase C very well, i.e. the BC interface has low energy. The relationship among the surface energies of the three phases determines the contact angle θ at the triple junction in an idealised situation where the surface is smooth.

The total energy balance is decreased due to the removal of the contact between the primary phase and the heterogeneous particle, and increased due to the formation of surface between the nucleating phase and the heterogeneous particle. This is illustrated in Figure 2-4 in which that portion of a sphere needed to form a cap with the required contact angle is shown for two cases: a material B which has a greater interfacial energy with C than does A ; and a material B which has a lesser interfacial energy with C than does A . A similar geometrical argument to that of Equations 2-1 and 2-2, including the effect of the circular interface of B and C , shows that the critical radius of these spherical particles is the same. This is expected as the local equilibrium at the AB surface should be the same despite the presence of C . However, it may be seen that the volume of B for such a critical particle is less than V_{sph} and depends upon θ .

The volume of the spherical cap is:

$$V_{cap} = \frac{\pi}{3} (2 - 3 \cos \theta + \cos^3 \theta) r_c^3 \quad (2-6)$$

and the ratio of this volume to the critical spherical volume is:

$$\frac{V_{cap}}{V_{sph}} = \frac{[2 - 3 \cos \theta + \cos^3 \theta]}{4} \quad (2-7)$$

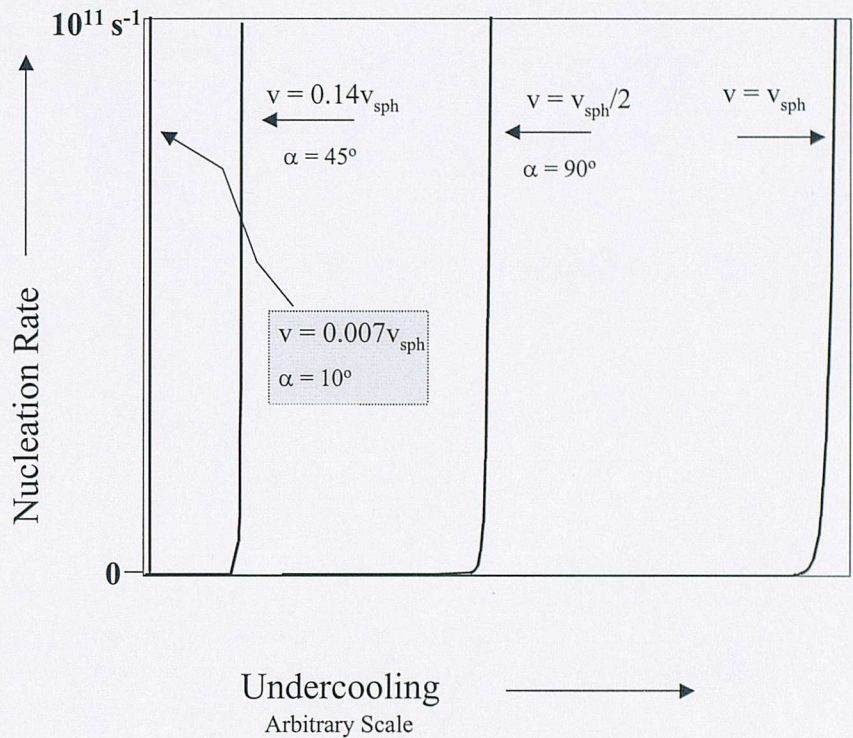


Figure 2-3. Nucleation rates for different critical volumes, as ratios of the critical volume for homogeneous nucleation of a sphere, calculated from the volume of conical sector of the sphere of apex angle 2α , illustrating the activity of such crevices in enhancing nucleation by decreasing the required undercooling.

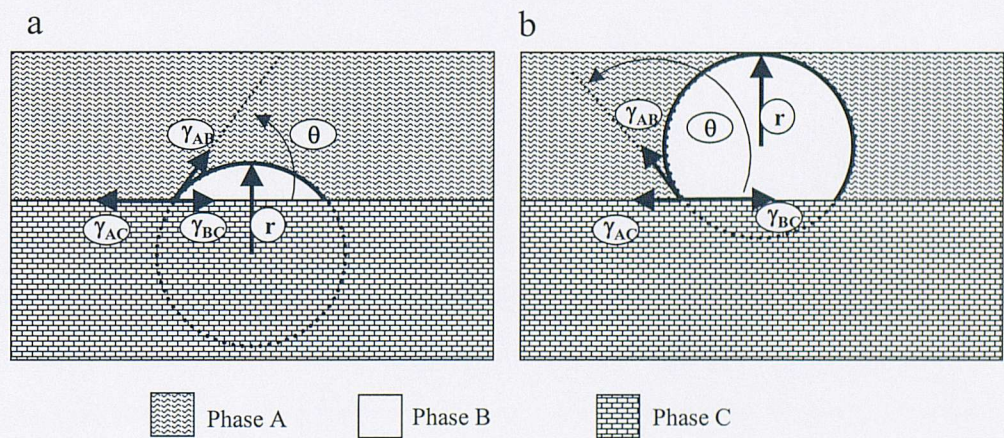


Figure 2-4. Schematic illustration of spherical nuclei of phase B forming from phase A on a planar surface of phase C – a heterogeneous nucleation site – for different relationships between the respective surface energies resulting in the contact angle θ . (a) $\gamma_{AC} > \gamma_{BC}$ and $\theta < 90^\circ$. (b) $\gamma_{AB} < \gamma_{BC}$ and $\theta > 90^\circ$.

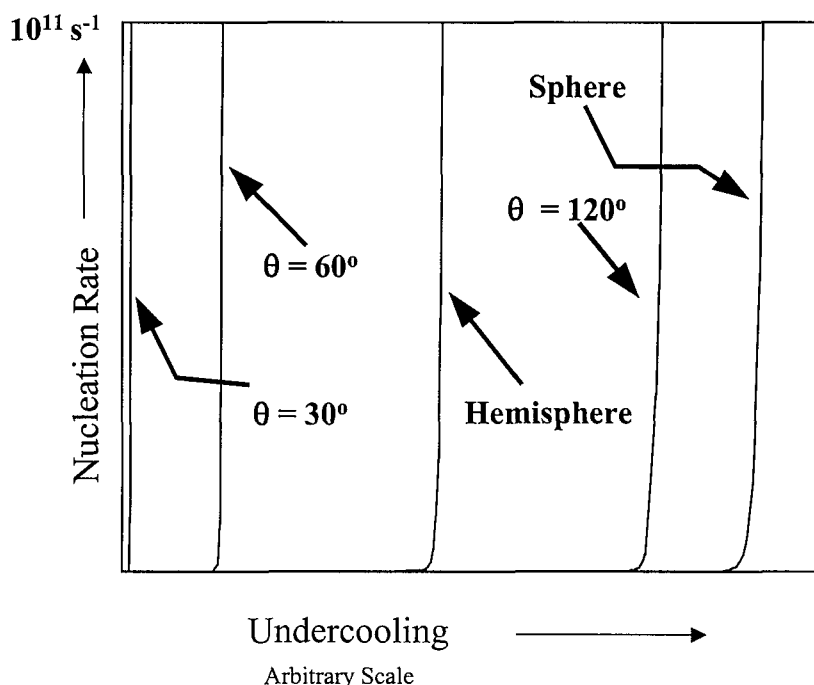


Figure 2-5. Nucleation rate curves for different critical volumes, as ratios of the critical volume for homogeneous nucleation of a sphere, calculated from the volume of a spherical cap with contact angle θ , illustrating the marked effect of the surface properties in enhancing nucleation.

Hence if the phase *B* wets the phase *C* moderately well with a contact angle of 60° , as shown in Figure 2-4(a), the cap volume will be $0.16(V_{sph})$ whereas if *B* wets *C* poorly with $\theta=120^\circ$ as shown in Figure 2-4(b), the ratio is 0.84; for a phase which wets *C* very well, with contact angle 10° , the ratio is 0.00017. The effect on the nucleation rate is illustrated in Figure 2-5 for angles of 120, 90, 60, and 30 degrees.

Thus, it may be seen that if the interfacial energy between the nucleating phase and the heterogeneous particle is greater than that between the primary phase and the particle, its activity will not be very great, whereas if the nucleating phase wets the heterogeneous particle moderately well, the effect is significant. The combination of these effects in a particular nucleating agent may be described as the activity or the effectiveness of the nucleating agent. This topic will be revisited with specific reference to gas phases nucleating within the liquid, in Section 2.3.

In casting practice, this behaviour can be used to advantage. In many cases it is desirable to produce castings with a uniform and small grain size, ensuring that the properties are also uniform within the casting and limiting the size of defects. This may be accomplished by adding grain refining inoculants to the melt. In aluminium alloys these often take the form of

alloys of Ti, B and Al which form titanium aluminides and titanium borides, which act to increase the rate of nucleation of the aluminium grains. The theoretical and experimental studies of this effect have been reviewed by McCartney and by Mohanty with particular reference to aluminium alloys [7, 8]. Greer *et al.* [9] propose a mechanism whereby the solid nucleates on the basal plane of tablet-shaped boride particles present in Ti-B grain refiners. If this layer of solid grows as a spherical cap, its radius must decrease as it grows. If the critical radius due to the energy balance as described above is greater than the minimum radius of the cap covering the particle surface, the particle cannot grow through this effective barrier. The observed nucleation event occurs when the conditions result in the critical radius decreasing below the minimum spherical cap radius for that particle which happens as the volume increases. The situation proposed is illustrated in Figure 2-6. Some TEM evidence for this mechanism has been given for the nucleation of the crystalline phase from a metallic glass phase [10].

This mechanism results in an instantaneous nucleation behaviour, in which each nucleus which can form does so as soon as the critical condition is met; because the event is not truly a nucleation event in the classical sense. The phase already exists as a layer upon the refiner substrate and is prevented from growing by the geometry. The distribution of nucleation events over temperature results from the distribution of nucleants with different critical temperatures at which the barrier to growth vanishes. In Greer's mechanism this is related to the size of the exposed basal plane of the particle of TiB_2 grain refiner.

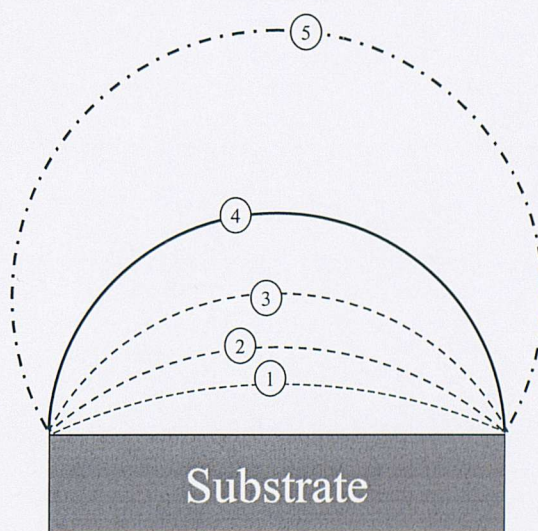


Figure 2-6. The growth sequence as suggested by Greer *et al.* for the formation of new grains from a refining substrate. Through successive stages particle surface decreases in radius as the particle grows from 1 to 4, then increases to number 5. After Greer *et al.* [9]

2.2.2. Growth

The mathematical study

The mathematical study of the growth of the solid phase leads to some difficult problems in theoretical mathematics. The mathematical problem is that of finding the minimum energy surface for the given conditions. Even for uniform isotropic conditions this gives rise to a problem known as Plateau's problem for which a general solution is not known.

In the simple case of a dilute binary alloy solidifying as a single phase (not congruently melting), we may observe three distinct regimes of behaviour at the solidification front: planar growth, cellular growth, and dendritic growth.

Because the solubility of the components is different in the solid and liquid, the composition of the solid phase is not the same as that of the liquid phase, and whichever component is less soluble in the solid phase will build up in the liquid, and this solute is said to be *rejected* at the solid-liquid interface. The solidification point for the solution thus formed will be different from that of the original liquid. A steady state may be reached in which the rate of diffusion of excess solute away from this interface equals the rate of rejection at the interface. In this situation, assuming the front is planar, the concentration profile of the solute may be calculated:

$$C(z) = C_{\infty} + \Delta C e^{\left(\frac{-vz}{D}\right)} \quad (2-8)$$

where $C(z)$ is the concentration as a function of distance from the interface z , C_{∞} is the concentration in the liquid far from the interface, ΔC is the difference between C_{∞} and the concentration in equilibrium with the solid, v is the velocity of the interface, and D is the diffusion coefficient of the solute in the solution. The ratio between the concentration in the solid and the concentration in the liquid with which it is in equilibrium is known as the *partition coefficient* and is usually designated k ; we may then find ΔC :

$$\Delta C = C_{\infty} - \frac{C_{\infty}}{k} \quad (2-9)$$

Gulliver-Scheil Equation

If one assumes no diffusion in the solid, and complete mixing in the liquid and negligible effect of surface curvature, the non-equilibrium freezing or *Gulliver-Scheil* equation [2, 11] will predict the solute concentration as related to the fraction solid, in the volume being considered:

$$C_s^* = kC_0(1 - f_s)^{(k-1)} \quad (2-10a)$$

i.e.

$$C_l = C_0 f_l^{(k-1)} \quad (2-10b)$$

in which the partition coefficient k is assumed to be constant.

If the solidification rate is great enough to be significant compared with the rate of diffusion, then the assumption that there is complete mixing in the liquid is no longer valid. The analysis of this situation was due to Tiller *et al.* [12] and resulted in the equation:

$$C_s = C_0 \left\{ (1 - k) \left[1 - \exp \left(-k \frac{v}{D} x \right) \right] + k \right\} \quad (2-11)$$

where x is the distance over which solidification has occurred.

This solute buildup, and the change in equilibrium freezing point arising from it, results in a situation known as constitutional supercooling [13] which causes the assumed planar interface to become unstable. In this situation, the difference between the applied temperature and the local freezing point of the liquid is greater at some distance in advance of the interface than it is at the interface. See Figure 2-7. Small perturbations in the shape of the interface then have a tendency to grow and the interface becomes cellular. This behaviour depends upon the growth velocity, the thermal gradient, the diffusion coefficient, the partition coefficient, and the relationship between concentration and solidus temperature.

At greater solidification velocities, the cellular structure becomes unstable due to constitutional undercooling in a narrower layer around the cell interface, and branches form giving rise to a dendritic structure, discussed below. At yet higher solidification rates, the effects of non-equilibrium solidification allowing solid to form with excess solute cause the cellular and planar solidification behaviour to re-emerge. This *rapid solidification* regime will not be covered in this project. Dendritic growth has been the subject of much study and has recently been discussed in reviews by Trivedi and Kurz [14] and Kerr and Kurz [15].

Constitutional Supercooling

The instability of a planar interface due to constitutional supercooling is illustrated in Figure 2-7, in which the local liquidus temperature T_l and the actual temperature T_q are shown in the upper diagrams for assumed planar fronts and the actual resulting interface is sketched in the lower diagrams. In the case of (a) the planar interface is stable whereas in (b) it is unstable and cells or dendrites will form and this will then alter the actual concentration.

During dendritic solidification, the solid forms as a series of arms projecting into the liquid, known as primary dendrite arms, with branches extending outward, known as secondary dendrite arms, as shown in Figure 2-8. In some situations further branchings (tertiary arms) may be observed. This morphology may form in a pure substance due to the buildup of latent heat released as solidification proceeds causing the instability of the interface, or in an alloy due primarily to the buildup of solute described above. Gulliver, Scheil and others have developed formulae for the distribution of solute during dendritic solidification, as described in standard textbooks [2-4, 6]. The early (1913) contribution of Gulliver to this field has recently been illuminated in an article by Glicksman and Hill [11]. If we assume pockets of liquid entrapped within the dendrite arms with little or no pathway for convection or diffusion to the bulk of liquid, then the Gulliver-Scheil equation, Equation 2-10, may be used. However, the structure of the dendrites is quite fine and the temperature is naturally very close to the melting point, so the assumption of no diffusion in the solid may not be very accurate.

Inclusion of Solid Diffusion

Brody and Flemings [16] have extended this treatment to include the effect of diffusion within the solid phase. Using the assumptions that the rate of dendrite thickening is a constant and neglecting any effect of shrinkage upon freezing, they developed the equation:

$$C_s^* = kC_0 \left(1 - \frac{f_s}{1 + \alpha k}\right)^{(k-1)} \quad (2-12)$$

Where the parameter α is related to the local solidification time θ_f :

$$\alpha = \frac{4D_s \theta_f}{\lambda^2} \quad (2-13)$$

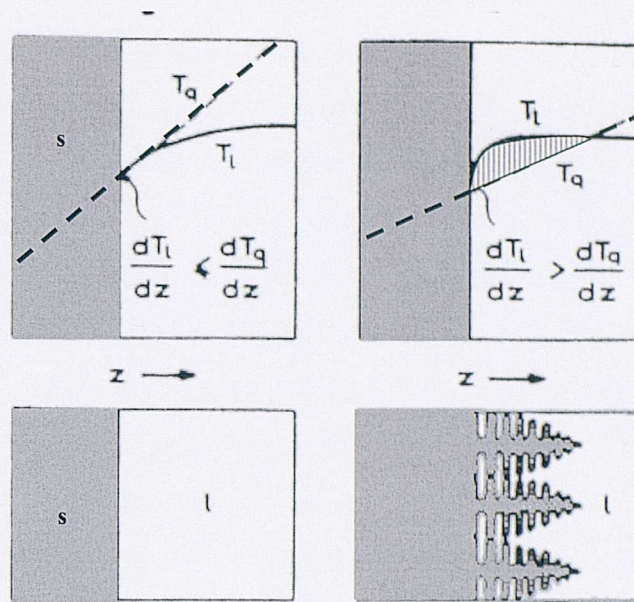


Figure 2-7. Schematic illustration of the effect of constitutional supercooling on a planar interface. (a) T_l is always less than T_q and the interface is stable. (b) T_l is greater than T_q in a region ahead of the interface and the planar interface is unstable, resulting in dendrites. After Kurz [3].

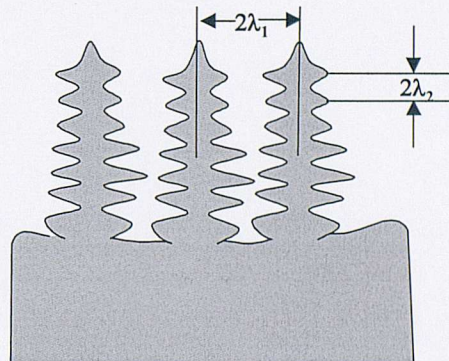


Figure 2-8. Schematic of solid dendrites in a liquid, illustrating the primary (λ_1) and secondary (λ_2) dendrite arm spacing.

In the same study, the authors also reported upon numerical solutions for this problem in which a non-constant partition coefficient was approximated by a series of linear segments. This type of treatment is feasible within the current project.

Much of the study of dendritic growth has focussed on predicting the geometry of the dendrites for given growth conditions. One approach in materials science has been to deduce correlations between the characteristic lengths for the important processes, and characteristic microstructural lengths.

The important processes and factors which affect the solidification process are the diffusion process, the evolution of latent heat and heat diffusion, the curvature of the solid-liquid

interface, the kinetics of attachment of atoms or molecules to the solid liquid interface, and fluid flow which will be discussed below with respect to porosity formation. For many cases, the situation can be simplified as one or more of these processes may be neglected. For example, in the case of directional solidification of binary alloys, the local effect of evolution of latent heat at the interface may often be much less than that of the effect of solute buildup, i.e. the length scale for diffusion of heat will be much larger than that for diffusion of solute and will not affect the interface shape on the latter scale. For many metals and alloys, the effect of attachment kinetics may be neglected, there is little barrier to the addition of new atoms to the solid and these materials solidify with non-faceted morphologies. This is not true for many intermetallic compounds and especially oxides and other compounds [17, 18], but this will not be covered in the present work. The atomic geometry of metals such as aluminium, having face-centred-cubic structures, is well suited to a cubical grid as the main dendritic growth directions formed at the axes of symmetry of octahedra formed by the close packed $\{111\}$ planes are in the $\langle 100 \rangle$ directions and form right angles with one another as observed and described by Chalmers [19]. For a material with non-cubic crystal structure, this would not be the case.

The characteristic scales for these processes are given by Trivedi and Kurz as: [14]

$$\text{Solute Diffusion Length: } l_d = D / v \quad (2-14)$$

$$\text{Thermal Diffusion Length: } l_t = \begin{cases} \frac{a_l}{v}; & \text{undercooled melts} \\ \frac{\Delta T_0}{G}; & \text{directional solidification} \end{cases} \quad (2-15)$$

$$\text{Capillarity Length: } d_0 = \begin{cases} \frac{\Gamma c_l}{\Delta H}; & \text{pure material} \\ \frac{\Gamma}{\Delta T_0}; & \text{alloy} \end{cases} \quad (2-16)$$

where D is the diffusion coefficient and a_l is the thermal diffusivity in the liquid, v is the growth velocity, ΔT_0 is the equilibrium freezing range of the alloy, G is the imposed temperature gradient in the case of directional solidification, c_l is the specific heat and ΔH the enthalpy of melting in the case of pure materials, and Γ is the ratio of interfacial energy to the entropy of fusion.

Correlations of the form:

$$L_i = A[l_d]^a[l_i]^b[d_o]^c \quad (2-17)$$

where L_i is the microstructural length scale of interest (i.e. the i^{th} length scale) are then sought. Of particular interest for this project are such correlations for the primary and secondary dendrite arm spacings (DAS) λ_1 and λ_2 as porosity forms within the structures having these length scales. Trivedi and Kurz [14] give the values of the exponents a , b , and c for these cases as summarised in Table I.

Table I. Exponents for Microstructural Length Scales of Interest. (Source: Reference [14])

Length Scale	a	b	c
Primary DAS	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$
Initial Secondary DAS	$\frac{1}{2}$	0	$\frac{1}{2}$
Final Secondary DAS	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$

The initial secondary dendrite arm differs from the final spacing due to the process of coarsening, whereby some arms grow at the expense of others.

The relationship between growth rate and temperature is somewhat elusive for dendritic solidification. The treatments in the literature, generally refinements of Ivanstov's 1947 steady-state analysis for a paraboloid shaped dendrite envelope, find a relationship between the undercooling and the Peclet number or dimensionless velocity $Pe = \nu R/2D_l$ of the form:

$$\Delta T_{tip} = \frac{k\Delta T_0 I\nu(Pe)}{1 - (1 - k)I\nu(Pe)} + \frac{2\Gamma}{R} \quad (2-18)$$

where $I\nu(P)$ is the Ivantsov [20] function appearing in the solution for the diffusion field around a paraboloid and may be found in the literature [3, 21] The function is defined as:

$$I\nu(Pe) = (Pe)\exp(Pe)E_i(Pe) \quad (2-19)$$

where E_i is the Eulerian exponential integral function $Ei(x) = \int_{-\infty}^x \frac{e^t}{t} dt = -\int_{-x}^{\infty} \frac{e^{-t}}{t} dt$ [22] and the

integration is chosen so as to not integrate the singularity at $t=0$.

This approach yields a continuum of possible solutions in which ν and R are related by Equation 2-18. If growth occurs at an extreme value for the stability or some other predictable condition, it is possible that the Ivantsov equations could be used to derive a growth rate versus temperature relationship.

In the case of eutectic alloys, the growth at the interface occurs in a coupled fashion; with alternating regions of the phases. In the case of regular eutectics, in which the growth occurs in the form of lamellae or rods, the diffusion and growth may be modelled by the equations of Jackson and Hunt [23] with the simplification that the interface is approximately planar, and that the ratio ζ of the volumes of the phases is a constant. Upon assuming that stable growth occurs at the *extremum* (or minimum undercooling) condition they arrive at the expression:

$$\frac{\Delta T^2}{\nu} = 4m^2 a' Q' \quad (2-20)$$

in which m depends upon the liquidus slopes, a' depends upon the ratio ζ , the Gibbs-Thompson coefficients for each phase, and the liquidus slopes, and Q' upon ζ , the diffusion coefficient and the initial concentration. Equation 2-20 may be simplified as:

$$\nu \propto \Delta T^2 \quad (2-21)$$

where the constant of proportionality is a modelling variable, as used by Rappaz [24] and Nastac [25]

Kurz, Giovanolli and Trivedi [26] developed a model (often referred to as the *KGT model*) for the diffusion limited growth of dendrites based on applying the Ivantsov solution to the stability criterion of Mullins and Sekerka [27] to predict the maximum growth rate of dendrites selected by Equation 2-18 which would be stable.

2.3. Porosity

The Formation of Porosity

During the solidification process, a number of different mechanisms contribute to the formation of porosity. The pressure within the liquid decreases as a result of restricted feeding. At the same time, the amount of dissolved gas in the liquid may increase due to rejection at the growing interface if the solubility of the gas is greater in the liquid than in the solid, which is usually the case. The supersaturation of the dissolved gas may increase as the temperature drops. These latter effects will raise the pressure at which the gas in a pore will be in equilibrium with the dissolved gas. If this pressure increases above the pressure in the liquid, then one would expect porosity to exist assuming equilibrium conditions. A number of authors [28, 29] have expressed this condition as follows, taking into account the pressure due to capillarity of a small round bubble:

$$\Pi_g \geq \Pi_a + \Pi_m + \Pi_s + \Pi_\gamma \quad (2-22)$$

where Π_g is the pressure in the gas, Π_a is the applied pressure, Π_m is the metallostatic head, Π_s is the pressure due to shrinkage (usually negative) and Π_γ is the pressure due to the surface tension and curvature of the bubble. (The symbol Π has been used to avoid confusion with P used for porosity in subsequent chapters.) If the term on the left is greater, an existing pore would grow.

This condition does not predict whether a pore will form if none exists. A nucleation event must occur as discussed below. Once a pore exists, it may grow if conditions are favourable; this depends upon the concentration and solubility of dissolved gas, the local pressure in the liquid, and the radius of curvature of the gas/liquid interface. In addition, the ability of the gas to enter the pore may be altered by impingement of the solid phase upon the pore surface or restriction of the diffusion path. The ability of liquid metal to enter the pore is often modelled by Darcy's law:

$$\mathbf{v} = -\frac{\kappa}{\mu f_l}(\nabla\Pi + \rho\mathbf{g}) \quad (2-23)$$

in which the velocity vector, $\mathbf{v}$, is related to the pressure gradient by the permeability, κ , and the viscosity μ ; and the effect of gravity $\mathbf{g}$ is included via the density ρ . As Poirier has noted [30], κ will in general be a tensor quantity but if the flow is isotropic it may be represented by a scalar. This is approximately the case in interdendritic flow, if the solid is equiaxed on a finer scale than the scale under consideration. If the scale of the grain structure is anisotropic, for example in a columnar microstructure, the scalar approximation may not be valid.

Nucleation of Gas Porosity

As described by Tiller *et al.*, [12] the solute buildup due to rejection will result in the formation of a second phase if the alloy system is suitable and if the initial concentration is great enough.

The theory of nucleation for gas phases is essentially the same as the general theory described above; the effect of pressure is more important, since the gas phase is compressible.

The mechanisms of nucleation of a vapour phase from a liquid have been extensively reviewed by Cole [31] as regards the boiling process, and most of the reasoning presented therein applies to vapour phase nucleating from a solution. The critical value of interest in this case is the concentration of the dissolved gas, which is related to the equilibrium vapour pressure in the case of a diatomic gas such as hydrogen, according to Sieverts' law [28]:

$$\frac{N}{N_{atm}} = \sqrt{\frac{\Pi}{\Pi_{atm}}} \quad (2-24)$$

In many treatments of the formation of gas porosity, the dissolved gas concentration and the equilibrium vapour pressure are used interchangeably; in other words, the equilibrium vapour pressure is used as the measure of the dissolved gas concentration. If this pressure exceeds the applied pressure, then the solution is supersaturated.

Whittenberger and Rhines [32] reviewed the mechanisms of porosity formation and presented experiments which show that porosity forms in the absence of shrinkage by using alloys of bismuth which expand upon solidification. Furthermore they could not find evidence of visible porosity in the absence of dissolved gas by using experiments in which the melts were heated to the boiling point in order to preferentially evaporate the dissolved gases. In addition they describe the interaction of the growing pores with the developing dendritic microstructure, describing how a pore constrained to extend linearly among dendrite arms might be expected to come into contact with more dissolved gas than a spherical pore in isolated liquid. The range of morphologies of pores formed by shrinkage-dominant effects versus gas-precipitation is summarised and classified into pores which nucleate primarily due to shrinkage forces lowering the pressure so that the dissolved gas may nucleate, and those in which the gas concentration is great enough to nucleate pores in the absence of shrinkage forces.

Homogeneous

Cole [31] reviews various experiments in which liquids are heated above their equilibrium boiling point. Apart from purity and cleanliness of the liquid, the method of containment must be very carefully designed in order to prevent the occurrence of heterogeneous nucleation. For example, a temperature gradient was established in a column of liquid, and drops of an immiscible second liquid of lower density were allowed to rise until they vaporised. In cyclopentane, the superheat achieved by this method was 110.2K, the ratio to the equilibrium vaporisation temperature being 1.4. This was quite close to the reported theoretical value of 109.3 K.

Homogeneous nucleation of phase transformations is difficult to observe experimentally because in most situations the nucleation barrier is overcome more easily by the process of heterogeneous nucleation due to the presence of particles of another phase. In this process, the

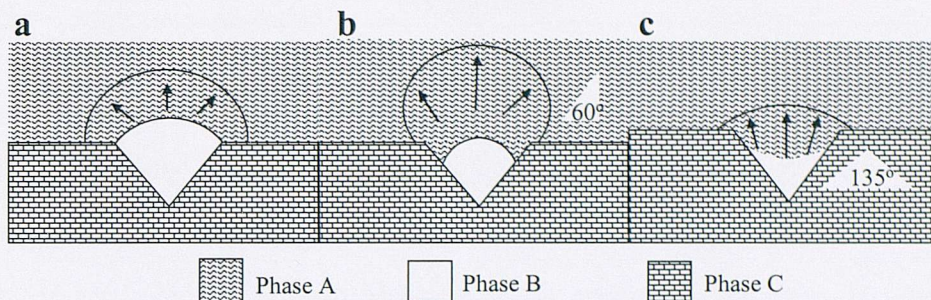


Figure 2-9. Some possible configurations for gas pockets in crevices. (a) 90° wetting angle. (b) 60° wetting angle. (c) 135° wetting angle. A possible position of the interface after growth of the gas phase is indicated in each case.

energy barrier to the formation of the new phase is reduced by the geometry of the heterogeneous particle and the surface energy balance.

Gas pores may also form from insoluble gas bubbles entrapped in inclusions or oxides [4]. In this case the nucleation barrier does not exist and pores grow from these existing bubbles. In certain cases the bubble may detach leaving behind a pocket of gas which repeats the process. Alternatively, the bubble may engulf the particle, and the number of pores formed in this way would be limited by the number of such particles. Once again this behaviour depends upon the surface energy between the particle and the melt, and additionally upon the geometry of the particle, as discussed above.

Gas Pockets

In the case of gas phase nucleating from liquid, another mechanism may play an important role in apparent heterogeneous nucleation. If the above mentioned (Section 2.2.1) crevices in heterogeneous particles contain pockets of insoluble gas, and the radius of these existing gas bubbles is above the critical radius they will grow. Some possible configurations for gas pockets in crevices are shown in Figure 2-9 for different wetting angles at the three phase junction. As shown in Figure 2-9c, the curvature at the interface with such a gas pocket may even be concave toward the liquid, resulting in a negative capillarity pressure.

Under certain situations the resulting bubble may detach from the original particle and leave behind a pocket of gas and hence the process repeats. Poirier [33] presents a calculation which determines under what conditions the bubble detaches, resulting in the equation:

$$r^3 + \frac{2\gamma}{\Pi_L} r^2 - \frac{3\varepsilon \Pi_G V_c}{4\pi \Pi_L} = 0. \quad (2-25)$$

This calculation assumes that the bubble detaches when the total volume in the detached bubble equals the volume of a nucleus of critical size, i.e. $\varepsilon=1$ but it is not explained why this

should be so. In fact, under the conditions described, in which the contact angle subtended by the gas phase between the other two phases is acute, it seems that in this case it would be energetically favourable for the particle to become entrapped in the bubble rather than detaching.

The theory of nucleation of gas bubbles in a supersaturated solution has been recently reviewed in an article by Jones *et al.* [34] in which they draw together these ideas about nucleation mechanisms. The degree of supersaturation obtainable before observed bubble generation in all but the most carefully contrived situations [31] is much less than that predicted by the classical homogeneous or heterogeneous theories, usually by 10 – 20 times. This may be due to pre-existing gas pockets, in agreement with the hypotheses of Poirier [33] and of Campbell [35] with respect to metallic melts. Jones *et al.* [34] have introduced a useful classification scheme for types of bubble nucleation based upon the study of bubbles forming in several types of systems, which is summarized as follows:

I. Classical homogeneous nucleation.

A bubble forms when the critical supersaturation at which the rate of formation of clusters equal to or greater than the critical radius is significant, is exceeded.

II. Classical heterogeneous nucleation.

A bubble forms as in I; however, the volume of a critical cluster is significantly reduced due to the presence of a substrate.

III. Pseudo-classical nucleation.

Prior to nucleation, a population of sub-critical gas pockets exists within the liquid which are rendered metastable by some mechanism. The authors hypothesize metastable micro-bubbles stabilized by surface-active molecules ('homogeneous pseudo-classical nucleation') or gas pockets associated with particles or container surfaces ('heterogeneous pseudo-classical nucleation'). This mechanism is pseudo-classical because the kinetics resemble those of classical nucleation but with reduced critical supersaturation which is not explained by the properties of the substrate. The curvature of the surface of the gas pockets is less than the critical curvature for growth, but local fluctuations cause some such pockets to grow in a similar manner to the growth of subcritical nuclei in the classical theory. This gives rise to a rate of

bubble formation which follows the classical form, but with greatly reduced critical degrees of supersaturation.

IV. Non- classical nucleation.

Again, a population of gas pockets exists within the liquid, but the curvature of their surfaces is equal to or larger than the critical curvature, and hence growth may proceed without overcoming any nucleation barrier.

In either of Type III or Type IV nucleation, the result is the formation of bubbles at much lower degrees of supersaturation than predicted by either Type I or Type II mechanisms. The Type IV mechanism is analogous to the free growth barrier mechanism proposed by Greer *et al.* [9] discussed in Section 2.2.1.

In metal systems, the difficulty of observing bubble formation directly has limited the amount of available results. Although experimental observation of gas pockets is particularly difficult in metals, several authors have suggested possible mechanisms. Campbell [4] suggests that, particularly in aluminium alloys, folded skins of oxide which form on the surface of the melt and subsequently become entrained may contain pockets of gas and aid the formation of porosity by this mechanism, and Fox and Campbell [35] reported observations of such films within aluminium, which could then produce a stream of bubbles by the Type IV mechanism at low degrees of supersaturation.

Mohanty *et al.* [36] propose a mechanism whereby the hydrogen is dramatically enhanced locally in the presence of an advancing solid-liquid interface by the buildup of dissolved hydrogen between the advancing interface and insoluble particles. The supersaturation becomes much greater in this region than that due to the average composition, and nucleation of the gas phase may take place when the apparent supersaturation is low. This mechanism depends upon the properties such as the surface physics and the diffusivity of hydrogen in the particle.

Solubility and Diffusivity

The solubility of hydrogen in aluminium has long been the subject of experimentation, with a variety of results, some of which are plotted in Figure 2-10. Talbot [28] reviewed the chemistry of hydrogen in solution in aluminium alloys and others, summarising the experimental results of several authors for the solubility of hydrogen in liquid and solid aluminium. The statistically generated consensus results are:

$$\log(S_l^0) = -\frac{2761}{T} + 2.768 \quad (2-26a)$$

$$\log(S_s^0) = -\frac{2580}{T} + 1.399 \quad (2-26b)$$

where S_l^0 is the solubility of hydrogen in pure liquid Al, S_s^0 is the solubility in pure solid Al, in units of ml/100g STP, and T is in degrees Kelvin.

Imabayashi *et al.* [37] used a rapid quenching technique and found a lower solubility, giving the formula:

$$\log(S_0) = \frac{-2392}{T} + 2.256; \quad (2-27)$$

which is in good agreement with recent results obtained by Szőkefalvi-Nagy *et al.* [38], using a continuous hydrogen activity (CHAPEL) measurement technique in which a porous carbon probe is inserted into the melt, and the hydrogen pressure above the probe is monitored. Figure 2-10 compares the results of these and some other published determinations of the solubility. The more recent determinations indicate a lower solubility than that determined by Ransley and Neufeld in 1948 [39]. Imabayashi *et al.* [37] suggest that the likely reason for this is that the linear correction used by Ransley for hydrogen absorption from the containment system is incorrect, giving a systematically higher value for the hydrogen in the sample.

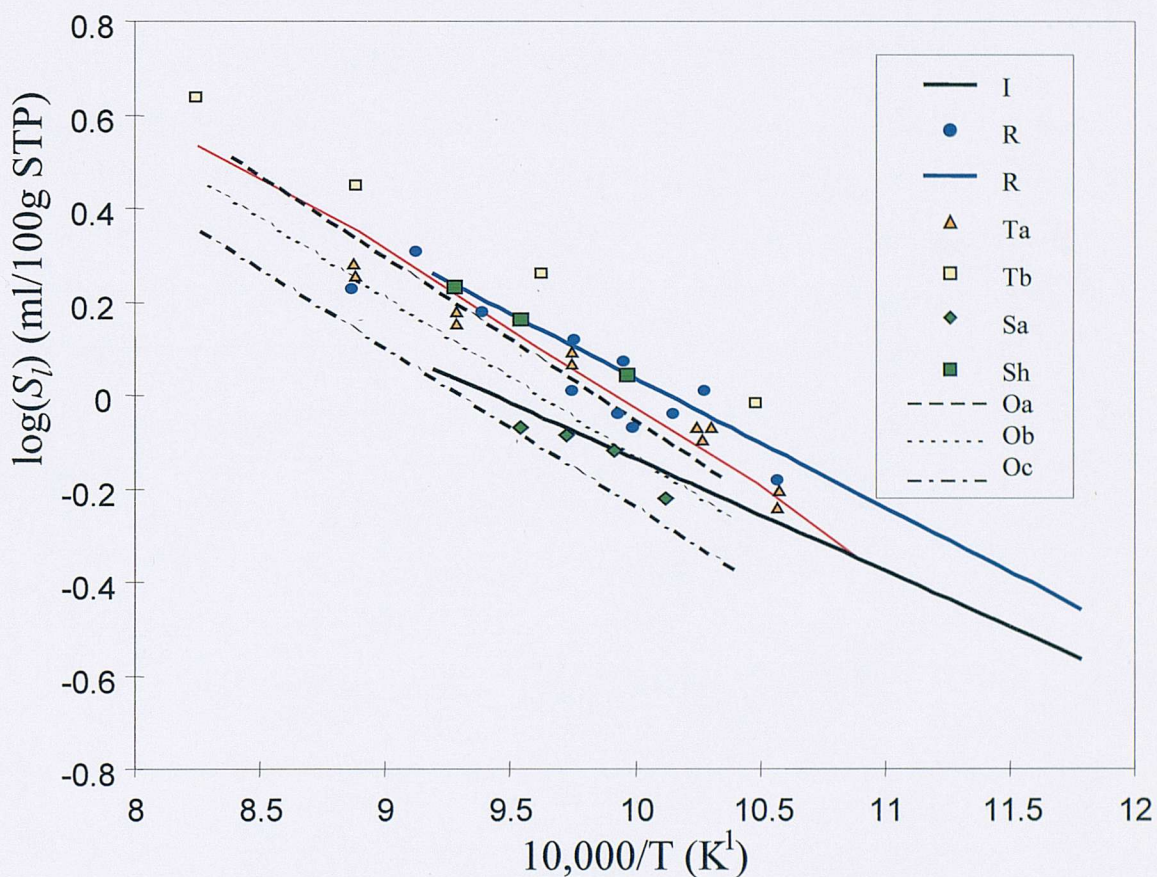


Figure 2-10. The results of several published determinations of the solubility of hydrogen in liquid aluminium. I: Imabayashi *et al.* [37], R: Ransley and Neufeld [39], points (circles) and formula (line) Ta: Talbot and Anyabalchi [40] Tb: Talbot [28] Sa: Szőkefalvi-Nagy *et al.* (in Air) Sb: Szőkefalvi-Nagy *et al.* (in Hydrogen) [38], Oa: Al-10Si Ob: Al-8Cu Oc: Al-16Cu [41] (After Talbot [28]).

The effect of alloying elements on the solubility of hydrogen has not been studied very much. Szőkefalvi-Nagy *et al.* [38] report some values for Al-Cu alloys, and Opie and Grant [41] give some results for Al-Cu alloys and Al-Si alloys. Both of these alloys have reduced solubility for H as indicated in Figure 2-10. The effect of Mg is generally known in the industry to increase the amount of hydrogen in the melt [21], and Doutre [42] has determined an empirical formula intended for use in calibrating the industrial hydrogen measurement equipment (ALSCAN):

$$S_l = S_l^0 \exp(0.0119C_l^{Si} - 0.0269C_l^{Cu} + 0.0170C_l^{Mg}) \quad (2-28)$$

showing that the solubility is increased by the presence of Mg. Additionally, it is generally observed in practice that hydrogen is absorbed more rapidly by Mg containing alloys, [21, 43] possibly due to the greater reactivity of Mg with atmospheric water vapour and a more permeable surface film. Although this mechanism is described in the literature [44, 45] there does not seem to be direct evidence for it so far.

Eichenauer and Markopolulos present results for the diffusivity of hydrogen in liquid and solid aluminium: [46]

$$D_l = 1.1 \times 10^{-5} \exp\left(-\frac{4922}{T}\right); \quad 633\text{K} < T < 873\text{K} \quad (2-29a)$$

$$D_s = 3.8 \times 10^{-6} \exp\left(-\frac{2315}{T}\right); \quad 1053\text{K} < T < 1273\text{K} \quad (2-29b)$$

in which the units are m^2/s .

Nucleation of Gas Porosity in Castings

Which of these mechanisms operate and to what degree within a cast metal certainly depends on many factors, such as alloy composition and formation of primary phases which may nucleate other phases, cleanliness and the composition and type of contaminating particles, the deliberate introduction of nucleating agents, casting geometry and feeding of liquid, and the amount of dissolved gas in the melt which in turn depends upon the processing history of the melt and the atmosphere in which the casting is carried out.

Kubo and Pehlke [47] assume that the pore nucleates in the root of secondary dendrite arms, apparently because that area appears to provide a narrow re-entrant cavity. Upon careful consideration of the true three dimensional dendrite shape, it seems that the location they specify is in fact a region of negative curvature that is only marginally more favourable as a nucleation site than any other point on the solid-liquid interface. Furthermore, the degree by

which such a cavity reduces the required supersaturation depends upon the wetting characteristics of the liquid on the solid – if the liquid wets the solid very well, there is little reduction in the required supersaturation and for a perfectly wetting liquid/solid system there is none [31].

Roy *et al.* [48] have presented an extensive study of the occurrence of porosity in aluminium alloys containing various amounts of Cu, Si and additives including Mn, Sr, and grain refiners; and at different levels of H content. They have used wedge moulds similar to that used by Tynelius [29] and used quantitative metallography to analyse 72 experimental castings. They suggest that there is nucleation of pores on the β -AlFe needle-like intermetallic phase, and that various intermetallic phases and ‘sludge’ act to physically restrict pore expansion. It should be possible to model this behaviour by allowing a nucleation function to depend upon the solidification characteristics of the β phase and compare with experiments. However, the association between the pores and the surface of the β needles is not conclusive evidence that these pores nucleated at this surface; they could have nucleated elsewhere and adhered to the surface due to favourable surface energy ratios, although those phases to which the pores do not adhere may be nucleation agents. In the absence of data about the surface energy of the melt- β and gas- β interfaces, it is not possible to calculate the degree of supersaturation required to nucleate at these apparently planar interfaces.

The analytical expression for the pressure in an individual bubble in an isotropic homogeneous environment may be derived from the geometry of the bubble [49], and for a sphere the relationship is:

$$\Pi = \Pi_0 + \frac{2\gamma}{r} \quad (2-30)$$

where Π is used to avoid confusion with the porosity fraction P_p used later on.

The growth of the gas pores then may be calculated if the concentration of gas in the liquid surrounding the pore is known, by equating the pressure in the gas and the equilibrium vapour pressure in the liquid, and including the excess pressure due to the curvature of the bubble surface, assuming an isolated spherical pore [33, 47, 50]:

$$\Pi_g - \Pi_l = \frac{2\gamma}{r} \quad (2-31a)$$

However, once the pore contacts the developing solid the assumption of a spherical pore is no longer valid; a situation such as that shown in Figure 2-11 will develop and the curvature will

depend upon the geometry of the solid. The more general form of Equation 2-31a may be used:

$$\Pi_g - \Pi_l = 2\gamma(1/r_1 + 1/r_2) \quad (2-31b)$$

where r_1 and r_2 are the principal radii of curvature for a non-spherical pore surface. Note that the radius may decrease as the pore grows as shown at point B in Figure 2-12 thus requiring an increase in pressure, or the pore may push through to an area where the radius of curvature increases as shown at point A, producing interconnected porosity described in Reference [32]. Lee and Hunt [51] have modelled such pores as hemispherically capped segmented cones in which the hemispherical sections are in contact with the liquid and were able to closely reproduce experimental results. The principal radii will then be limited by either the primary (A) or secondary (B) dendrite arm spacings.

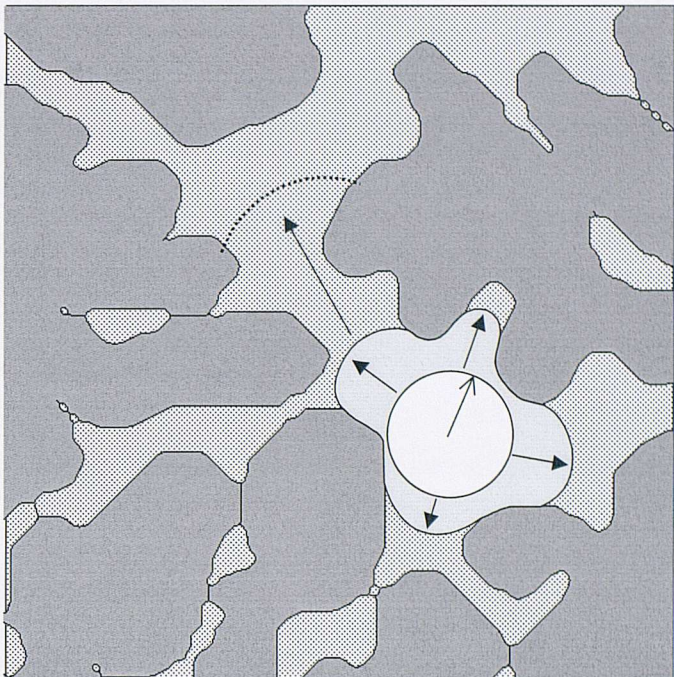


Figure 2-11 Schematic of a gas pore growing within a dendritic network of the solid phase. Note that as the pore size increases, the radius of curvature of the gas-liquid interface may decrease or increase as a result of the solid phase geometry.

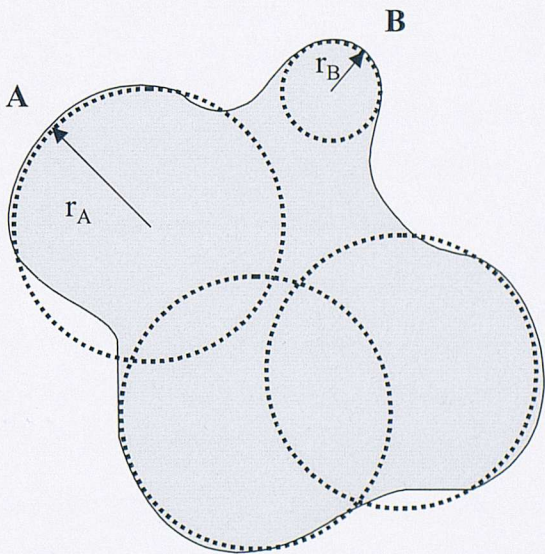


Figure 2-12. Schematic of the hypothetical pore illustrated in Figure 2-11 showing the approximately equivalent circles for the gas-liquid interfaces. The radius of the gas-liquid interface at B is much less than that at A, therefore a greater gas pressure is required to extend the gas into the interdentritic region at B.

2.4. Models of Bubble and Pore Growth

Once a bubble has nucleated, it will change in size and pressure due to transport of gas between the bubble and its surroundings. The problem of gas bubble growth in a diffusing medium may be represented mathematically as a Stefan problem [52], in which a differential equation is to be satisfied in a two-phase domain and the location of the boundary between the phases is to be determined as part of the solution. In three dimensions, this boundary may take on any shape, but in a simplified one-dimensional formulation the boundary is a single point, and the position of this point as a function of time is the required solution. If spherical symmetry is assumed, and assuming all properties are homogeneous and constant in each phase, a solution may be found using a general similarity solution of the type:

$$r_i^2 = t, \quad (2-32)$$

where r_i represents a suitably transformed co-ordinate of the boundary position and t is time. Scriven [53] obtained a particular solution of this form for the growth of carbon dioxide bubbles in water, including the effect of radial convection in the liquid:

$$r = 2\beta(Dt)^{0.5}, \quad (2-33)$$

where r is the radius of the bubble, D is the diffusion coefficient, and β is a dimensionless growth coefficient.

However, this solution requires the aforementioned simplifications, which will generally not apply in a solidifying melt. The distributions of hydrogen solubility, diffusivity, and concentration are, in general, neither constant nor spherically symmetric about a bubble. The volume averaged solubility and diffusivity depend upon the degree of solidification and the alloy composition. The hydrogen concentration depends upon the rejection of hydrogen as solid forms and its incorporation into existing bubbles, and therefore upon the distance between them. The growing bubble may impinge upon the solid and hence its growth will be restricted. The bubble may also move, or liquid may flow past the bubble carrying dissolved gas.

Numerical modelling of some of these processes during the growth of a single bubble has been reported by the current author and colleagues [54, 55] assuming a regular array of bubbles which may be approximated by spherical symmetry. The results illustrated the dependence of the growth function on the system size, which may be interpreted as an

averaged distance to the neighbouring bubbles. In a population of growing bubbles, those bubbles that have more and closer neighbours will have a smaller effective system size and, on this basis alone, would have slower growth rates.

2.5. Experiments in Pore Growth and Characterisation

Although most studies of porosity in castings have been qualitative in nature, in recent years the use of digital image analysis has allowed quantitative analysis of porosity. Perhaps the first extensive study was that by Fang *et al.* [56] in which sections of rectangular end-chilled castings of Al 4.7Mg and Al356 alloys were analysed for porosity as a function of the cooling rate and thermal gradient, for various contents of hydrogen. Among their conclusions were that lower hydrogen content, higher cooling rate and addition of grain refiner reduce the amount of porosity and the pore size. However they did not consider the interaction of various parameters or whether the parameter correlations observed were direct, or due to some other unobserved parameter

Nagaumi *et al.* [57] studied the porosity in an industrially produced direct-chill cast slab of Al 4.4 Wt%Mg. They used Darcy's law to predict the distribution of porosity resulting from the shrinkage and feeding restriction caused by solidification to explain the observed increase in porosity towards the centre of the slab.

Parametric Study

In order to obtain some quantitative understanding of the effects of various conditions upon the formation of porosity in aluminium castings, Tynelius [58] and Tynelius *et al.* [29] undertook studies in which a number of parameters were varied within and among samples, and the resulting porosity quantified. The resulting data were subjected to extensive statistical analysis using multiple regression techniques, which allowed the estimation of which parameters affected which features. In order to obtain a significant sample of different parameters within a small number of castings, a special casting geometry was developed. This consisted of a steel mould for a wedge-shaped billet, in which the sides of the mould were adjustable so as to allow a range of different wedge angles. This provided a range of cooling rates and thermal gradients within a single sample, and by varying the wedge angle, the ratio between the cooling rate and thermal gradient could be altered. This also had the effect of altering the local solidification time; one of the features of the statistical analysis they used was the ability to determine the significance of each parameter and the interaction between them upon the final outcome. They determined that hydrogen content was the strongest predictor of all individual variables studied; however, the correlations were better if the

combinations of hydrogen content and other variables were considered in the analysis. The best correlation was that using the combined hydrogen and solidification time variables. Of the thermal parameters, the solidus velocity and the local solidification time were determined to be the best predictors of porosity.

Transparent Alloys

The direct study of solidification phenomena in metals is complicated by the high temperatures and opacity of the melt. Jackson and Hunt [23] used the transparent organic materials CBr_4 and C_2Cl_6 , which form a eutectic system with non-faceting solidification behaviour, to observe the formation of microstructures with visible light. Akamatsu *et al.* [59] have observed the formation of gas porosity in purified CBr_4 - C_2Cl_6 alloys processed in air. The studies were carried out at solidification velocities in the cellular growth regime, and often but not always resulted in coupled growth of the vapour and solid phases forming long 'fingers' or 'wormholes' of gas in between solidification cells. The gas pores were observed to nucleate within the intercellular grooves, but not necessarily at the very bottom (cold end) of the groove. Given that the greatest supersaturation of gas would be expected at the extreme base of the groove, the authors suggested two explanations for their observation: that the pores nucleate at the root but travel by capillary action or convection before they are large enough to observe, or that the density of nucleation sites is low enough that often, by chance, no nucleant particle was located at the base of the groove.

in situ radiography

In order to obtain first-hand understanding of the formation of porosity, Lee & Hunt [60] developed a technique for direct observation of porosity formation during solidification of aluminium alloys. They used a vertical temperature gradient furnace with a microfocal X-ray unit (X-ray temperature gradient stage, or XTGS), imaging the solidification zone directly. By using the images as captured by a digital video camera, the radius of observed pores could be measured and tracked as a function of temperature, as shown in Figure 2-13. In this way, a large number of pore formation events could be observed and analysed. The radii of observed pores were extrapolated to zero in order to estimate the temperature at which the nucleation event occurred.

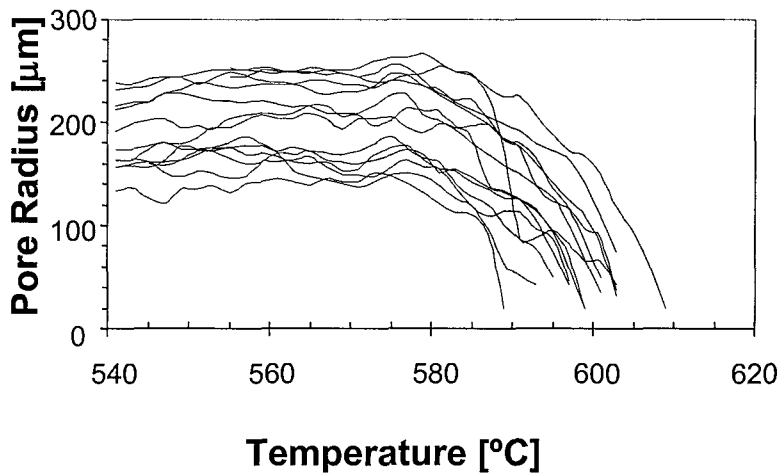


Figure 2-13. An example of the data obtained by the method of Lee and Hunt [60] showing the radii of individual pores as solidification proceeds and the temperature decreases.

Through statistical analysis of these data, empirical rate functions have been determined for the formation of porosity, although these are believed to represent the interaction of several factors, particularly the competition between the mechanisms of depletion of dissolved gas by the growth of existing pores and the increase in the level of gas due to the combined effects of solute rejection and solubility decrease as a function of temperature [61]. It is hoped that these various factors currently lumped together in the statistics can be separated and properly understood, partly through the course of the current work.

Lee *et al.* [60-62] estimated the degree of supersaturation obtained during the formation of bubbles in Al-Cu and Al-Si alloys. They found very small degrees of supersaturation, suggesting the nucleation mechanism is Type III or IV. The low levels of supersaturation could also indicate that local buildup of hydrogen plays a role.

2.6. Computational Modelling

The modelling of porosity formation in castings requires the consideration of several interacting processes. As the temperature decreases, the volume of metal changes, and the solubility of dissolved gases changes. Once solidification begins, there is usually a large change in volume (generally a decrease) associated with the phase change, partitioning of solute (if any) and dissolved gas between the phases, evolution of latent heat. The liquid will flow to compensate for the volume change, this will be restricted to various degrees by the solid which has formed. The subject has recently been reviewed by Lee *et al.* [63]

Modelling of porosity

Some authors [47, 50] have attempted to quantify the pressure drop due to shrinkage by applying Darcy's flow model, Equation 2-23, to the interdendritic region. Darcy's model was originally developed from observations of the increased pressure required to propel a fluid through a larger number of smaller diameter pipes compared to a smaller number of larger pipes totalling the same cross sectional area. Hence a non-uniform region may be modelled as a series of pipes and from this is calculated a permeability factor representing the ratio of pressure drop to flow rate. In castings, the dendrite arm spacing is used to calculate the permeability since the fluid is constrained to flow in the channels between the dendrites. If the flow is parallel to the solidification direction, the primary dendrite arm spacing is the relevant dimension; if it is perpendicular then the secondary dendrite arm spacing must be factored in [30]. In many treatments, a single isotropic permeability is assumed. From this, a pressure drop may be calculated from the rheological properties of the melt.

In certain cases, the growth of pores is driven by diffusion of dissolved gas into the pore and not by the drop in pressure due to shrinkage. Whittenberger and Rhines [32] observed that the presence of dissolved gas is always necessary for the formation of porosity, and that porosity forms in the presence of dissolved gas even if there is no shrinkage. The formation of a pore in the body of the casting requires some nucleation event, as described above in Section 2.3. Finite difference techniques combined with iterative simulations [61] have been used to model the diffusion equation assuming regularly spaced pores surrounded by an evolving semi-solid region. As the solid forms, the hydrogen concentration is increased by partition and the effective diffusion coefficient in the multiphase region is decreased. This model was shown to give good agreement with experiments in which the pressure drop due to the restricted interdendritic feeding was negligible.

Kubo & Pehlke [47] have modelled the formation of porosity in plate castings and compared the results with experiment in both Al 4.5% Cu and 0.014%C steel, taking into account shrinkage due to restricted fluid flow and the evolution of gas into existing pores. They confined the modelling to the regime of interdendritic fluid flow and solved the heat and fluid transfer equations using finite difference schemes, assuming Darcy flow. The build up of dissolved Cu is assumed to follow the Gulliver-Scheil equation in the AlCu alloy whereas the build-up of dissolved C is assumed to follow the Lever Rule in the case of steel in order to calculate the amount of solid as a function of temperature. The "amount of porosity" is

calculated from the solution thermodynamics and conservation of H (in the Al alloy) and CO (in the steel alloy) at each time step, according to the following equations for heat balance:

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho C} \left(\frac{\partial^2 T}{\partial t^2} + \frac{\partial^2 T}{\partial t^2} \right) - \frac{L}{C} \frac{\partial f_l}{\partial t}; \quad (2-34)$$

mass balance:

$$\left(\frac{\rho_s}{\rho_l} - 1 \right) \frac{\partial f_l}{\partial t} - \frac{\partial f_l v_x}{\partial x} - \frac{\partial f_l v_y}{\partial y} + \frac{\partial f_v}{\partial t} = 0; \quad (2-35)$$

and conservation of hydrogen:

$$[H_0] = (1 - f_l)[H_s] + f_l[H_l] + \alpha_H \frac{\Pi_g f_v}{T}; \quad (2-36)$$

where α_H is given as $\frac{27300}{f_l \rho_l + f_s \rho_s}$, and additionally Darcy's law, Equation 2-23, and the pressure equilibrium within the bubble, Equation 2-31a.

However, the nucleation step is not modelled; in fact it seems unclear what criterion or rule the authors used to decide when porosity begins to form. Possibly they assume that if there is any supersaturation at all then a nucleus must form, or if the amount of supersaturation is such that a pore of the assumed diameter equal to the secondary dendrite arm spacing is at equilibrium, then the pore forms. Their model assumes that the porosity nucleates upon the surface of the developing solid, which is one possible site mentioned by Whittenberger and Rhines [32].

In contrast to the situation assumed by Kubo and Pehlke, in which pores are assumed to nucleate at the root of secondary dendrite arms, Poirier [33] states that the heterogeneous nucleation at the solid liquid interface is nil. This view seems the more reasonable; the liquid metal wets its solid completely as Poirier goes on to describe, and so the pressure required to nucleate a gas bubble at the surface would be of the same order as that for homogeneous nucleation.

Fang and Granger [50] model the pore-liquid-dendrite system as a concentric sphere with the pore at the centre and a solid shell at the outside. The gas concentration increases within the liquid due to rejection but is assumed to be uniform within the liquid. The relationship between the solid sphere inner radius, the hydrogen concentration, and the pore radius is solved assuming the Gulliver-Scheil equation for the solid growth and full gas diffusion in the

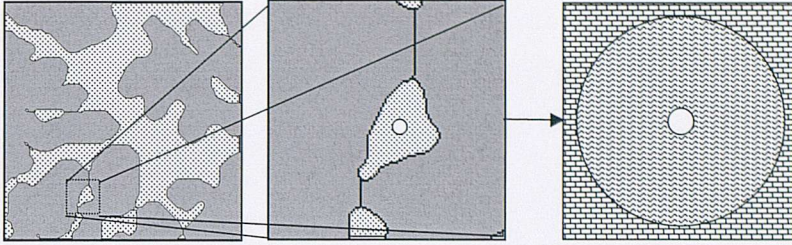


Figure 2-14. Schematic illustrating the simplification used by Fang & Granger [50]. A pocket of liquid surrounded by solid is modelled as a sphere. The gas pore grows at the centre of this sphere.

solid and liquid. For this model a nucleus of one micron was assumed to exist at the centre of the sphere, and the authors showed that the final pore size did not vary significantly with the assumed pore nucleus size. The amount of liquid included within the cell is proportional to the primary dendrite arm spacing λ_1 by the constant η :

$$R_0 = \eta \lambda_1 \quad (2-37)$$

and this constant is varied as part of their study. This factor relates to the specific geometry of the dendrites, and whether they cause pockets of liquid to be isolated in this fashion, and at what stage this happens. This is likely to depend upon the composition of the alloy in that the magnitude of the freezing range and the partition coefficient should affect the shape of the dendrites for a particular cooling rate. A schematic of this assumption compared to a dendritic structure is shown in Figure 2-14.

This model neglects the effect of shrinkage. The results are found to be in good agreement with experimentally observed trends and hence indicate that shrinkage is not always critical in determining the form of the relationship between cooling rate and gas porosity formation.

2.7. Cellular Automata

2.7.1. General

In a cellular automata model, it is assumed that the behaviour of each small region or *cell* is influenced only by the conditions within that region and the conditions in neighbouring regions.

The domain of the model is divided into a grid of cells. Each cell may be thought of as a simple computer or automaton which calculates the new state of the cell based upon the states of itself and its neighbouring cells, hence the name of the technique. Simulation time is also divided into discrete steps; each automaton calculates the state of its cell at each time step as a

function of the states of the cells in its neighbourhood at previous time steps according to a set of transition rules which is the same for all cells. The majority of cellular automata models limit the transition rule to depend upon the immediately preceding time step, and upon the nearest neighbours only.

The use of cellular automata techniques goes back to the earliest days of computer simulation.

History

In the early 1950's, John von Neumann proposed a two-dimensional cellular automaton with neighbourhood and transition rules in a manuscript dealing with the possibility of designing machines which could reproduce themselves. His description is quite clear and concise:

In this chapter we will develop the first model that possesses the potentialities of logical and constructive universality and of self reproduction This model is based on a crystalline medium; we will be able to construct it in two dimensions and to use the quadratic (regular) lattice. Each lattice point of this crystal will be able to assume a finite number of different states (say N states) and its behavior will be described (or controlled) by an unambiguous transition rule, covering all transitions between these states, as affected by the states of the immediate neighbors [64].

Von Neumann goes on to propose a system of cellular automata on a square grid in which each automata may have 29 states in order to simulate the behaviour of neural systems with resting, excited, refractory and other states available. The transition rules depend upon only the immediately preceding time step and on neighbours which are immediately horizontal or vertical neighbours. This particular four-cell neighbourhood dependence is therefore known as the *von Neumann neighbourhood*. An alternative neighbourhood often used is that consisting of the 3x3 square surrounding the cell including the diagonal neighbours; this is called the *Moore neighbourhood*.

Conway, Gardner, Life

In the early 1970's, mathematician John Conway developed a simple set of CA rules that exhibited unusual behaviour: quite simple patterns would evolve into unpredictable forms. The rules were published and popularised through the 'Mathematical Games' column of Martin Gardner in Scientific American magazine [65]. The experimentation with CA rules quickly became a fad among those with access to computer equipment at that time, mostly university students in math and engineering subjects, prompting Time Magazine to report:

...millions of dollars in valuable computer time may already have been wasted by the game's growing horde of fanatics ... [66]*

Wolfram

This was essentially a curiosity until the work of Wolfram [67] on the classification of the behaviours resulting from various transition rules. This work showed that the complex type of behaviour was equivalent to computation, therefore the automata represented by these grids of dots could in principle solve any problem solvable by digital computer. Cellular automata were classified into four categories based upon the information required to predict the evolution of the configuration based upon an initial state:

The final state is independent of the initial state (e.g. all patterns disappear)

The final state of a particular site is dependent upon the initial values of sites in a limited region (e.g. all patterns give rise to simple repeating patterns)

The behaviour is chaotic and appears random but “it is conjectured that the value...may be determined by a simple algorithm”

The behaviour may not be predicted by any algorithm of lesser complexity than the cellular automaton itself, i.e. the system is equivalent to universal computation

Rucker [68] has extended and slightly modified this classification and his classification is given in Table II

Table II. Cellular Automata Classification (after Rucker [68])

Rucker Type	Wolfram Type	Behaviour
I	1	Dies out
II a	2	Fixed Space Pattern
I Ib	2	Periodic Cycle
IIIa	4	Self-organising scrolls
IIIb	4	Moving gliders or globs
IV	3	Chaotic seething

The understanding that such CA models could be equivalent to universal computation led to the development of interest for the modelling of physical systems [69] and the building of

* It is hoped that the current project, among others, will help to show that this time was not in fact wasted.

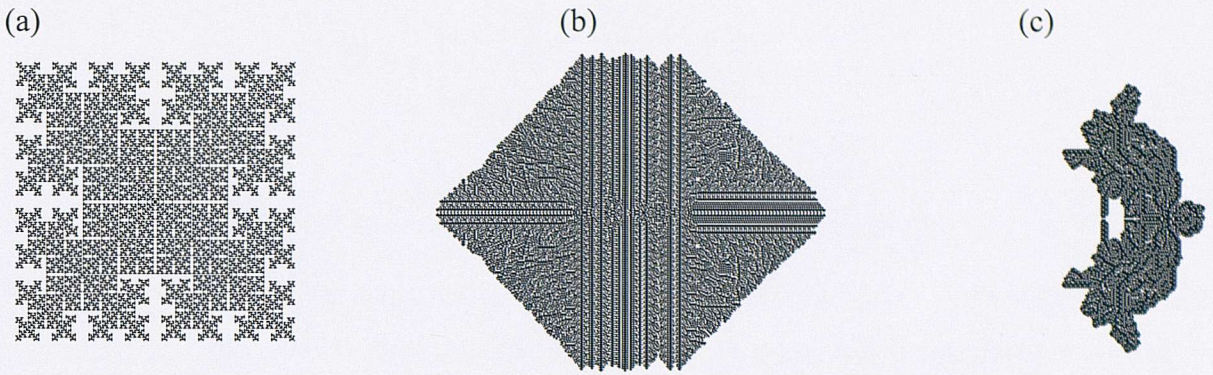


Figure 2-15. Some patterns generated by simple binary cellular automata rules in the 2-d Moore neighbourhood. (a) “Exactly 1 Solidification;” (b) “Exactly 2 Solidification;” (c) “Exactly 3 Solidification;” Figures produced using MC-Life software.[†]

special purpose devices for running CA models [70] Such models are often seen to complement existing types of numerical models rather than superseding them [71].

CA models often produce patterns that are seen to resemble patterns formed in nature, and therefore it is natural to expect that these models may be used to model the processes that form such patterns. See for example the patterns shown in Figure 2-15 which have dendritic form. There remains a gulf of understanding as to why these patterns appear similar and how the processes that form the one relate to those that form the other. Part of the explanation lies in the study of complex dynamics generally, in which it is shown that pattern formation is a fundamental feature of non-equilibrium complex systems. The interested reader is referred to Nicolis and Prigogine [72]. However, this observation does not produce any predictive results and the apparent similarity between certain CA systems and certain natural systems may say nothing more than that both systems are complex.

Another form of classification, primarily of a range of cellular automata fitting into Type II a, has been published by Gravner and Griffeaths [73], based upon the type of rules and the limiting shape taken by the pattern for large times. Of particular interest are those rules which the authors classify as ‘solidification rules’ in which any cell once transformed to a ‘solid’ state, remains so. The examples in Figure 2-15 are of this type; (a) uses the “Exactly 1”, (b) uses the “Exactly 2” and (c) uses the “Exactly 3” solidification rule. The “Exactly n ” rule is:

[†] By Mirek Wojtowicz, available for download at: <http://www.mirwoj.opus.chelm.pl>

$$\Xi(c) = \begin{cases} 1, \text{ if } \left(\sum_i \Xi(n_i) = 1 \right) \text{ or } \Xi(c) = 1; \\ 0, \text{ otherwise,} \end{cases} \quad (2-38)$$

Where Ξ refers to the (binary) state of a cell and n_i are the neighbours of the cell.

The CA's studied by Gravner and Griffeaths [73] are all of the discrete binary type in that the cell state is either 0 or 1 and the transition depends upon the sum of the states of the neighbours, part of the analysis allows for a general neighbourhood of any number of cells. The analysis is useful in that it discusses the features leading to grid-dependant limiting shape for most cellular automata of this type. However, as it is a purely mathematical treatment of the set-theoretical aspects of these models, it does not relate these different neighbour combinations allowing transformation to any physical process. Although some rules seem to produce patterns which resemble patterns formed during solidification, if these cannot be related to process variables they do not have predictive value.

Continuous Valued CA

Most of the studies in physics, mathematics and computer science on the behaviour of cellular automata have focussed on the behaviour of finite-state automata, similar to those proposed by von Neumann and largely inspired by the popularisation of Conway's 'life' by Gardner [65] and others [74]. In these models, each cell may take on a very limited number of different values. The rule defining the new state from the neighbour states may be arithmetic, Boolean, or some combination. Most generally the rule is a mapping from all possible combinations of neighbour states to all permitted new states. Even for a very small number of permitted states, the set of all such mappings is quite large. For example, if only two states are allowed, called "on" and "off" or "alive" and "dead" and the 8-cell two-dimensional Moore neighbourhood is considered, then the total number of possible transition rules is 2^{2^9} ; as there are 2^9 possible combinations of neighbour + self states and each of these combinations may result in a new state of either "on" or "off". This is certainly a very large number, and even though it may be reduced significantly by symmetry and other equivalencies, there is still a large variety of possible behaviours; and in 3 dimensions the number is somewhat greater, $2^{2^{27}}$ or approximately $10^{40,000,000}$. It is not known whether the classifications of Wolfram and Rucker may easily be extended to three-dimensional CA. Rucker [68] points out that repeating spiral patterns similar to those observed in the Belusov-Zhabotinsky reaction [72] occur in two

dimensional CA but no similar behaviour may be observed in one-dimensional CA, and it is possible that new types of behaviour that are unexpected may occur in three dimensional CA models.

Ostrov and Rucker [75] have introduced the term ‘Continuous Valued Cellular Automata’ to describe cellular automata schemes in which the states associated with each cell are not limited to a finite set, as described by Wolfram [76] but instead can take on any real-number value or set of values. This describes the technique used by Fermi, Pasta and Ulam, above, and much of the work done in cellular automata simulation in materials processing, described below. Of course, they hasten to point out that any digital implementation is of necessity limited to a finite set of states determined by the precision of the digital data storage used. This is far greater than the 2, 8, or 256 state automata often considered, and represents a boundary or overlap between cellular automata techniques and finite difference techniques.

Through comparison of modelling experiments in which the precision of the floating-point numbers used was artificially reduced, Rucker [75, 77] was able to determine that the known behaviour of linear waves was reproduced over a large number of time steps if the full precision was used. If the precision was reduced the linear waves would die out rapidly. At full (single) precision the wave would persist for millions of time steps but if only 3 decimal places were stored the wave would die out after 800 updates. Thus it was concluded that the precision of floating-point numbers was sufficient to allow simulation of the non-linear wave equations investigated, over the 10^5 to 10^6 time steps considered.

For some CA implementations the difference from finite difference implementations may reflect how the model is developed rather than the final mathematical form. To develop a finite-difference model, one must describe the system to be modelled by differential equations, which then may be discretised by one of a number of standard or special techniques. To develop a CA model, one must describe the behaviour of each part of the system by difference equations based on the interaction between neighbouring parts. Thus one can create a model for a system without deriving the differential equations which describe it – and in some cases deriving these equations might be impossible. In fact, in the original FPU publication, the differential equations for the non-linear spring-mass system are not derived; the authors simply state:

The corresponding partial differential equation obtained by letting the number of particles become infinite is the usual wave equation plus nonlinear terms of a complicated nature [78].

The model they had developed was simulating a non-linear wave system, but they had not taken the step of developing a system of differential equations to describe the system. The usual process of developing an analytical model and then finding a numerical method to solve it was inverted; the model described a behaviour which was only later analysed mathematically. Some 40 years later, Ostrov and Rucker [75] derived the equations for quadratic and cubic coupling assuming small non-linearities.

The power of the CA technique lies in this feature. A highly complex system may be modelled by relatively simple elements, when constructing an analytical description of the whole system is intractable. However, the requirement is a great deal of data storage space.

A variety of different neighbourhoods for application of CA rules have been used by various researchers [24, 79, 80]. Figure 2-16 illustrates some of these which are of interest to the current project. In addition to the von Neumann and Moore neighbourhoods described above, the hexagonal neighbourhood, three-dimensional von Neumann-type and Moore-type neighbourhoods, and the pseudo-2d hybrid neighbourhood are shown.

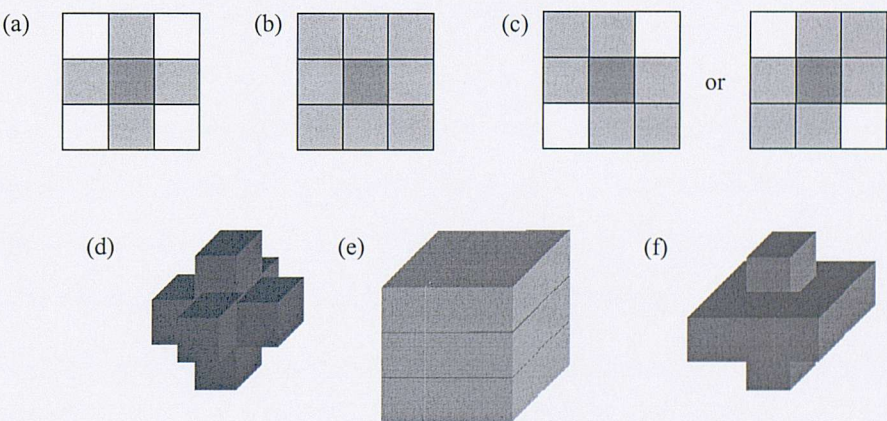


Figure 2-16. Some cellular automata neighbourhoods: (a) The 4-cell or von Neumann neighbourhood; (b) The 8-cell or Moore neighbourhood; (c) the left- and right- handed hexagonal neighbourhoods; (d) the 3-dimensional 6-cell von Neumann neighbourhood; (e) the 3-dimensional 26-cell Moore neighbourhood; (f) the 3-dimensional hybrid 10-cell neighbourhood.

CA techniques started to come into use for qualitative modelling of complex systems contemporaneously with the dramatic increase in computer data storage space in recent years.

2.7.2. *Materials Modelling*

Much of the application of CA techniques to materials modelling has been to eliminate the mathematical complexity of analytically modelling the shapes and distributions of features which occur during materials processing by using the cellular domain to actually simulate the boundaries. For example, Charbon *et al.* [81] used a model that was not really a cellular automaton model, in that the rules were not local, but used a cellular array to store the shapes of simulated grains during solidification. In this model, each cell was updated depending upon its radial distance from a nucleus point. Essentially, several instances of an analytical growth model were run simultaneously and the cellular automata would determine where and when impingement was occurring, obviating the need for an averaged impingement factor in the analytical equations.

The CA technique has been used for the modelling of solid state phenomena, such as recrystallization and grain growth during annealing. Certainly the phenomenological reasoning of the model is clear – each part of the solid is in a certain state, changing to another state under certain conditions including whether it is in contact with material of that other state. Hesselbarth and Göbel [80] have presented a model of this type for the simulation of recrystallization and compared to the classical JMAK analytical model using a 2 dimensional cellular grid. Marx *et al.* [82] have recently presented a CA recrystallization model which includes the effect of recovery in unrecrystallised grains, and presents statistical analysis of the computer generated microstructures.

Nucleation

Perhaps the most intense exploration of cellular automata based techniques for solidification modelling has been by the group of M. Rappaz *et al.* at the Ecole Polytechnique de Lausanne. They have published a number of works using cellular automaton and similar techniques to simulate the developing microstructure during solidification.

Charbon & Rappaz [81] compare a ‘probabilistic’ cellular-array model with a ‘deterministic’ time-stepping mathematical model. In the probabilistic model, the domain is divided into cubic cells, a calculated number of nuclei are distributed randomly among the cells, and solidification proceeds according to the model of Jackson & Hunt [23] (Equation 2-20). The latent heat released is determined by the number of cells which solidify. In this work the solidification rule is not local; the radius of each grain is calculated from the model of Jackson

& Hunt [23], and those cells within this calculated radius of an original nucleus are solidified and become part of that grain unless they are already solid and hence part of another grain.

The nucleation is calculated from the empirically based model of Zou [83], in which the grain density versus temperature is fitted to a Gaussian distribution. The equation used is:

$$N(\Delta T) = N_{\max} \frac{1}{T_s \sqrt{2\pi}} \int_0^{\Delta T} \exp \left[-\frac{1}{2} \left(\frac{\Delta T' - T_n}{T_s} \right)^2 \right] d(\Delta T') \quad (2-39)$$

derived using the assumption that the grain density observed in a sample rapidly cooled to a particular temperature is due strictly to nucleation. Here ΔT is the undercooling, and $N_{\max}$, T_n and T_s are the height, mean and standard deviation of the Gaussian, respectively.

This model incorporates the observation that fewer sites appeared to be activated in samples cooled to lower temperatures below T_n . In fact it seems that the rapid growth of the grains first nucleated would overtake nuclei which are activated only at the lower temperature, and hence this behaviour is due to a combination of nucleation and growth. In the cellular model, this nucleation equation was applied by calculating the change in undercooling at each step and determining the integral of Equation 2-39 for that interval in order to calculate the expected number of nuclei per unit volume, N . From this the probability that a nucleus will appear in any particular cell was determined, and a random number test was applied to each cell and nuclei placed accordingly.

The cellular array simply kept track of which volume elements have solidified according to the underlying mathematical model; the volume elements do not solidify based upon the conditions prevailing at that location. Therefore a very good agreement with the mathematical 'deterministic' model should be expected and indeed was reported by the authors. The advantage of the cellular array model is that by keeping track of all liquid and solid volume elements, the effect of impingement is easily taken into account without necessitating assumptions about the degree of overlap of the spherical grains and the corresponding impingement factor. Hence the mathematics is simplified but the amount of data to be stored is increased.

Oldfield [84] proposed a different form for an equation relating the undercooling to the formation of nuclei, based upon observations of eutectic cast iron. The nucleation increases continuously as the undercooling increases, the observed levelling-off of the number of grains as the material is cooled more rapidly is considered to be a result of the rapidity of the growth

of the solid phase under these conditions. Nucleants which should become active at large undercoolings have no chance because they have already been incorporated into the solid phase. The dependence he observed was:

$$N(\Delta T) = A\Delta T^2 \quad (2-40)$$

This mechanism agrees with the recent experimental observations of Tronche and Greer [10] who measured the distribution of particle sizes of grain refiner observed at the centre of grains compared to the distribution of all refiner particles observed. The former population occupies only the upper slope of the distribution curve, indicating that only the most active nucleants actually result in nucleation events. The instantaneous nucleation at a critical temperature for each nucleus assumed by Oldfield may be explained by a growth mechanism (rather than true nucleation) as described by Greer *et al.* [9] for grain refined aluminium.

Orientation

To improve the degree of accuracy in models of solidification it is necessary to incorporate the effects of crystalline anisotropy and of surface curvature. However, for cellular automata models these effects have proven difficult to incorporate whilst maintaining the locality of the rules, because the information available from only the nearest neighbours is limited. A few different techniques which have been used for handling these parameters are outlined below.

Rappaz and Gandin [24] have modelled the effect of preferential growth along crystallographic axes by applying a “dendrite tip correction”. This is based on the observation that the square-grid growth of cellular automata proceeds along the axes of the grid as illustrated in Figure 2-17, and that transforming additional cells in the regions shown with light grey moves the apparent growth direction to the preferred growth direction. The disadvantage of this technique is that it requires that each transformation event depend upon the distance and direction of that volume element from the nucleation event site, for which it is difficult to envision a physical mechanism. Furthermore, as the authors themselves point out, [85] this requires that the temperature be uniform or this distance would not equal the distance of growth in every direction.

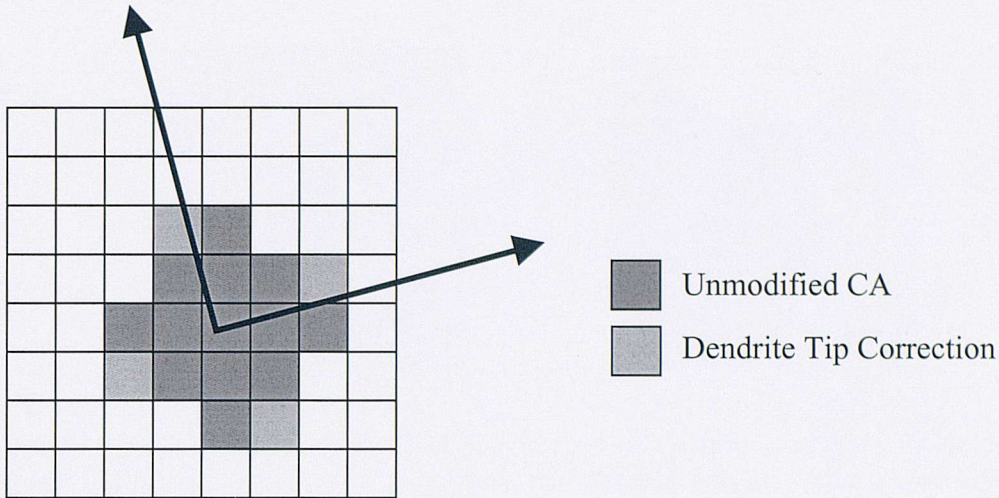


Figure 2-17. The dendrite tip correction of Rappaz and Gandin locates regions as shown (light grey) which are offset from the grid direction toward the preferred growth direction of the grain by storing the original nucleation location for each grain. After Rappaz and Gandin [24].

Gandin and Rappaz [85] have used a “decentred square” in two dimensions and a “decentred octahedron” in three dimensions to account for crystallographic orientation. This is essentially a refinement of the procedure in Reference [81] in that the nucleation point for each grain is recorded and used to determine if certain cells are captured; if they fall within this decentred zone around the nucleus. The size of the ‘decentred’ zone is limited and when the maximum size is reached, the centre is then shifted. This helps to account for non-uniform temperature distributions, since the size of the zone is in part determined by the local temperature. Wang [86] has begun to develop a combined decentred-square and diffusion model to include the effects of composition into such a model. Warnken *et al.* [87] have developed a multiple grid method in which each grain is simulated in its own grid, thus allowing its preferred growth directions to be aligned with the grid, but the overall microstructure is represented in a master grid; each grain grid is rotated at some angle to the master grid accounting for the crystallographic orientation of the grain.

Nastac *et al.* [25] applied a probabilistic test to a cellular array model. The shape of the solid-liquid interface in directional remelting processes was calculated using a macro model of mass and energy transport within the ingot. A probabilistic neighbourhood selection scheme was used in which the von Neumann, Moore and hexagonal neighbourhoods were chosen with probabilities depending upon the orientation of the grain. For angles less than 15° the Moore neighbourhood was used; for angles greater than 30° the von Neumann neighbourhood was used, and for angles between these limits a 50% probability determined by random

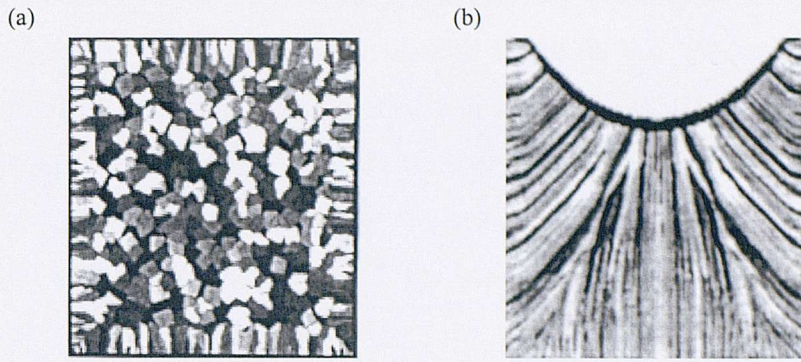


Figure 2-18. Examples of published results of cellular automata modelling of solidification. (a) Image due to Rappaz and Gandin [24] in which the container wall includes additional nuclei, and (b) image due to Nastac [25] from a model in which orientation effects were included.

numbers was used to select between left- and right- handed hexagonal neighbourhoods, along the lines of what Davies [79] has done for recrystallization models. In addition, a ‘selective randomisation procedure’ was used in which cells were constrained to transform only when their position corresponded to the growth direction normal to the calculated solid-liquid interface. This cellular array model allows the visualisation of the grain structure, but insofar as the growth characteristics seem to be entirely determined by the macro model it appears to predict little additional information. However, this rule is local in that it does not depend upon the original nucleation location.

The results due to Rappaz and Gandin [24] and those of Nastac *et al.* [25] are reproduced in Figure 2-18 (a) and (b) respectively.

Curvature

In order to incorporate the effect of surface curvature on the equilibrium of interfaces through the Gibbs-Thomson effect, some way of determining the local curvature within the model is required, whilst keeping the information associated with each cell to a minimum. Napolitano and Sanders [88] and Kremeyer [89] have presented two-dimensional models of morphological developments of dendrites, in liquid-solid systems only, using somewhat different approaches to include the combined effects upon solidification of solute build-up and interface curvature in CA models.

The former approach [88] assigns a probability of growth, i.e. transformation, to each cell which is a function of the undercooling, the solute concentration, and the curvature, including anisotropy. Based upon a random number choice, a cell is set to solid with a probability p and the excess solute is distributed among the “available neighbouring cells”, presumably the cells

bordering upon the newly solid cell, which are themselves liquid. The solute field is updated using an implicit finite difference scheme though it seems that an explicit scheme would suffice. In the case of large arrays and especially three dimensional arrays of cells, this could drastically increase the modelling time. Furthermore it is not made clear how the local curvature is determined from the values of the cellular array, it simply being stated that it depends upon H , which is the contribution due to interfacial curvature but not how this is found.

The latter approach [89] was to calculate the curvature based upon a weighted sum of the cells in the neighbourhood, using either a Moore neighbourhood or the extended 5x5 neighbourhood to allow a finer graduation of possible calculated curvature. The templates were chosen so that the modelled curvature would be low for flat surfaces and high for sharp projections, in other words there is qualitative behaviour similar to curvature. Two example templates and the results from the model (for rapid solidification) are reproduced in Figure 2-19. The transformation rule requires that a minimum of three neighbours be solid for a cell to transform, and that the cell be in an undercooled state according to its temperature and solute concentration values. However, no real or simplified phase diagram is presented so it is not clear how this criterion is determined. Furthermore the apparent rationale for using the three neighbour transformation rule (see Figure 2-15) was that it gave better results, but this was not related to any observed or hypothesised physical behaviour. The criterion for freezing depending upon solute concentration, combined with this three neighbour rule, allowed interdendritic regions to remain in the liquid state for all time.

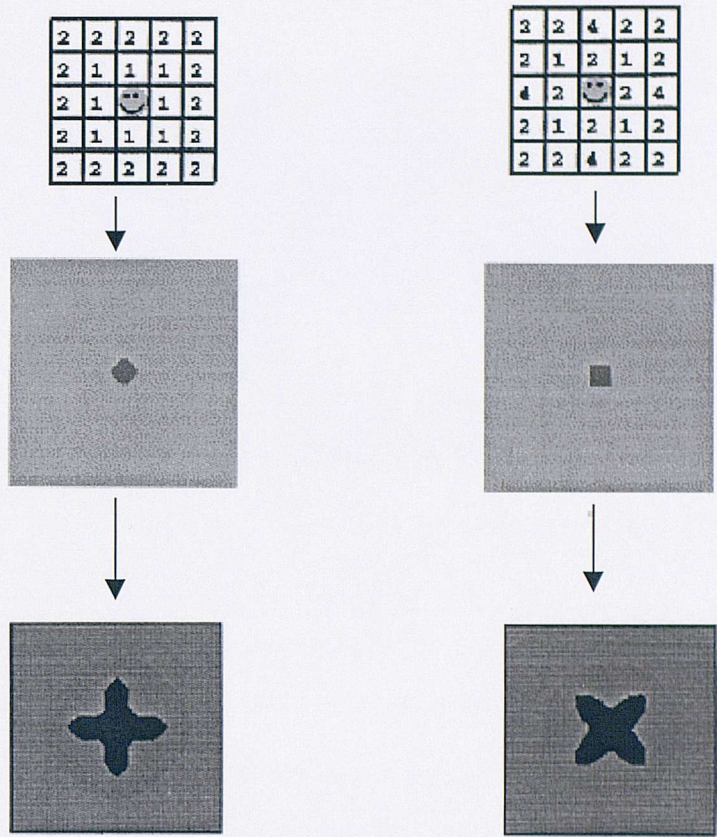


Figure 2-19. The template method for curvature estimation; the neighbours are “weighted” according to their position with respect to the current cell (smiley face), and the results of two different template choices. Source: Reference [89].

Porosity

Huang and Conley [90, 91] have presented a CA model incorporating porosity and unidirectional coupling to a macro-model, simulating the casting of A356 alloy in a permanent mould, with hydrogen dissolved in the melt. In their model they assume instantaneous nucleation of the solid phase by distributing a pre-calculated number of nuclei throughout a two-dimensional CA grid. The macro-model determines the temperature distribution for repeated cycles of casting in a permanent mould. The coupling is unidirectional in that this information is used by the CA micromodel but no information from the micromodel is used by the macromodel.

The number of grain nuclei formed is thus determined by the cooling rate calculated by the macromodel according to the equation:

$$N = K_1 + K_2 \dot{T} + K_3 \left(\dot{T} \right)^2 \tag{2-41}$$

where differentiation with respect to time is indicated by the over-dot and the K_i are empirical constants.

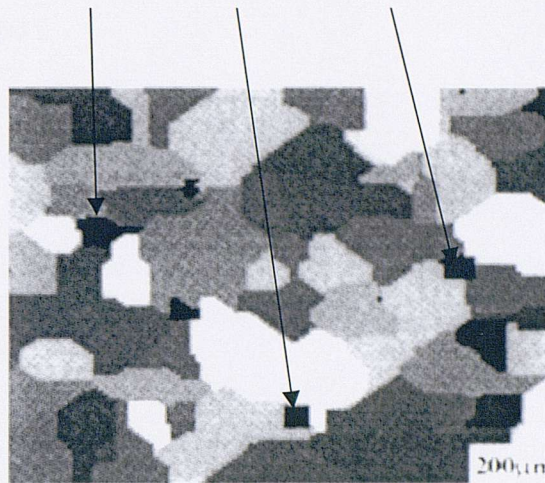


Figure 2-20. The results of a CA shrinkage porosity model due to Huang and Conley for the initial case yielding the highest porosity. Note that pores larger than 1 cell appear (arrowed). Source: Reference [90].

The growth of grains proceeds by capturing of nearest neighbours in the von Neumann neighbourhood, though the formula used to determine the growth rate is not given.

The model assumes nucleation of the vapour phase upon the growing solid front, and furthermore assumes no significant barrier to nucleation. If the calculated pressure allows a pore of (two-dimensional) area equal to one CA cell to be in equilibrium with the liquid phase, the pore is formed by randomly assigning a cell at the solid liquid interface to the vapour phase. It appears from the results given, Figure 2-20, that the vapour or porosity cells may grow into neighbouring cells however the precise mechanism for determining this growth is not explained.

The model also assumes complete diffusion of hydrogen within the liquid and hence any change in diffusion characteristics due to formation of solid or change in temperature are not modelled. The model was applied to multiple cycles of permanent mould casting, and was able to reproduce the reduction in percent porosity observed in experiments.

3. MODEL THEORY

The computational model developed during the course of this work combines a number of sub-models for the most important processes which affect the development of gas porosity in aluminium castings. The model may be broadly divided into the grain growth submodel and the pore growth submodel. Each of these includes submodels for the nucleation and growth of the solid or gas phases respectively, and the diffusion of the dissolved species.

A combined cellular automata and finite difference model for grain growth [92, 93] was developed to simulate the formation of the developing dendritic microstructure during solidification of a binary alloy. The diffusion of the alloy solute and the dissolved gas is calculated by a finite difference technique. This grain growth submodel is similar in concept to that presented by other authors [24, 94-96] although the length scale is generally greater and several details of the implementation differ. The growth model is coupled to a cellular automata model which simulates the growth of gas bubbles which appear as pores in the final structure .

The model begins with all the cells in a liquid state. The cells may transform to the partly solid 'growing' state either by a nucleation event or due to growth proceeding from a neighbouring cell. Each of these processes requires some degree of undercooling in the cell. When the amount of solid in a cell increases, the dissolved solutes are partitioned between the solid and liquid phases. The change in the solute concentration affects the degree of undercooling and hence feeds back to the nucleation and growth processes. At the same time, the solutes diffuse through the liquid and solid.

Similarly, a pore may form in a cell by a nucleation event, and a pore may expand into a neighbouring cell if the degree of gas concentration allows. The details of the techniques used to simulate the processes of nucleation and growth of the solid phase, diffusion, and nucleation and growth of the gas phase will be described in this chapter.

3.1. Solidification: Cellular Automata for Grain Nucleation and Growth

The cellular automaton model for the nucleation and growth of the solid phase is designed to simulate the competing processes of nucleation and growth during the transformation from liquid to solid phase in a binary alloy system, and simulate the shape of the growing grains. The main systems of interest are the AlSi and the AlMg systems. The Al-rich portions of these phase diagrams are shown in Figure 3-1.

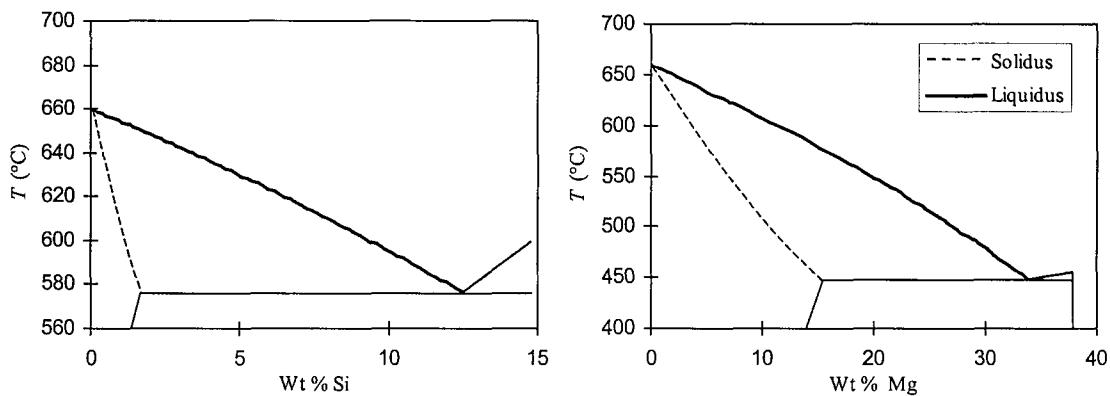


Figure 3-1. The phase diagrams for the Al-rich part of the systems of interest, (a) the Al-Si system, after [97] (b) the Al-Mg system, after [98].

3.1.1. Nucleation

The nucleation is determined stochastically, representing the essentially random process of finding a nucleating agent in a particular volume of liquid when the conditions favour the nucleation event. The probability that a nucleus forms in a particular cell is determined by the degree of undercooling in that cell as suggested by the theories of heterogeneous nucleation discussed in Chapter 2. However, the precise nature of the nucleating agents was treated as an unknown. It is assumed that a population of potential nucleation sites exists within the domain such that each site may initiate nucleation if exposed to liquid with undercooling T_n . Each potential nucleus in the domain has a randomly selected value of T_n . Three possible models for the relationship between the nucleation probability density $\bar{n}_n$ and the nucleation undercooling T_n were implemented:

- Simple step nucleation, in which there was no nucleation below a critical undercooling T_c and a constant probability of nucleation above T_c up to a maximum undercooling T_{max} ;
- Quadratic law nucleation, in which the probability of nucleation depends upon a quadratic function of the undercooling, as suggested by Oldfield [84], if the undercooling exceeds T_c ;
- Gaussian law nucleation, in which the probability of nucleation depends upon a normal distribution function as suggested by Rappaz [24] and Zou [83] about a mean undercooling T_c having a standard deviation of T_σ .

Each of the methods was implemented by determining the total number of nuclei N_n for the domain volume V and creating N_n potential nuclei. A random value of T_n is assigned to each nucleus such that the distribution obeys the chosen rule, and then each nucleus is randomly assigned to a cell. Each cell may be assigned at most one nucleus.

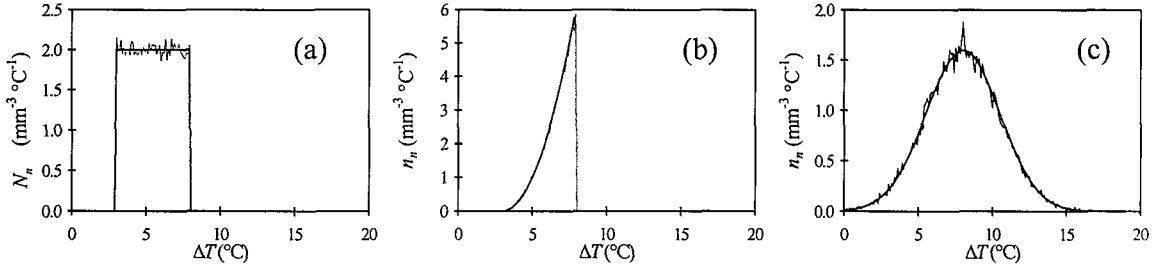


Figure 3-2. Graphs of the implemented probability distributions for nucleation. (a) Simple step nucleation (b) Quadratic nucleation (c) Gaussian nucleation. The black curves show the relationship chosen for the nucleation probability density N_n and the grey curves show example implementations.

The step distribution is formed by selecting the T_n between T_c and a maximum undercooling T_{max} ,

$$T_n = T_c + (T_{max} - T_c)\xi, \quad (3-1)$$

where ξ is a randomly generated number between 0 and 1.

The quadratic function was formed by choosing random numbers and transforming according to the inverse of the integral of the desired quadratic function:

$$T_n = T_c + (T_{max} - T_c)\sqrt[3]{\xi}. \quad (3-2)$$

The Gaussian distribution was formed by applying the Box-Mueller algorithm [99] to produce random values having a normal deviation with from the mean.

During solidification, the undercooling in each cell is calculated from the temperature and the solute concentration in the cell. If the undercooling in a fully liquid cell containing a nucleus exceeds T_n for that cell, then the fraction solid is set to a small value (10^{-6}) and the cell may grow. If growth from neighbouring solid has already begun in the cell, nucleation is not allowed, thus accounting for the extinction of nucleation sites due to incorporation into the solid phase.

3.1.2. Growth

The growth model incorporates the following assumptions:

- The alloy solute diffusivity is constant in the solid and liquid.
- The solubility of the alloy solute is described by a linearised phase diagram.
- Shrinkage is not considered.
- An effective diffusion coefficient is used for a partly-solid cell.
- Ternary diffusion effects between the alloy solute and the gas solute are negligible.

The growth of the solid involves two separate stages in the CA model: firstly the averaged evolution within a cell; and secondly the propagation of the solid from one cell to the next.

The growth is first estimated by:

$$v = \alpha_g \Delta T^2, \quad (3-3)$$

where v is the growth velocity, ΔT is the undercooling and α_g is a grain growth constant of $9.85 \times 10^{-5} \text{ ms}^{-1} \text{K}^{-1}$ based upon the treatment by Rappaz and Gandin [24] of the KGT model [26]. The growth velocity, v , is used to determine an initial estimate of the change in the fraction solid index, f_s , within a cell at each timestep. Using this estimate, the partitioning of solute was determined in growing cells using:

$$C_s = kC_l, \quad (3-4a)$$

and the lever rule:

$$C = f_s C_s + f_l C_l, \quad (3-4b)$$

where C is the solute concentration and the subscripts s and l denote the solid and liquid phases, respectively.

The diffusion equation:

$$\frac{\partial C}{\partial t} = \nabla \cdot D \nabla C, \quad (3-5)$$

was combined with Equations 3-4a and 3-4b and an effective diffusion coefficient, D_e (calculated using the rule of mixtures), to form the governing equation:

$$\frac{\partial}{\partial t} (f_s k C_l + (1 - f_s) C_l) = \nabla \cdot D_e \nabla C_l, \quad (3-6)$$

where k is the partition coefficient. This equation was solved using an explicit finite-difference scheme upon the same grid as the cellular automaton, according to the finite difference formulation:

$$C_l^n = \frac{\varphi^o}{\varphi^n} C_l^o + \frac{1}{\alpha^n} \Sigma^o \quad (3-7)$$

where $\varphi = (1-(1-k)f_s)$, superscript o refers to the ‘old’ value and n to the ‘new’ value, and Σ^o represents the sum of the diffusive fluxes from the neighbouring cells:

$$\Sigma^o = \frac{\Delta t}{\Delta x^2} \sum_{i=1}^6 D_e^i (C_l^o - C_l^i) \quad (3-8)$$

where the index i refers to each of the six neighbours in the three-dimensional grid of cells. The effective diffusivity between each pair of cells D_e^i is taken as the average of the effective diffusivities in the central cell and the neighbour cell, to ensure conservation of solute.

This causes the dendrite tips to grow into the melt at a rate governed by the KGT model as approximated by Equation 3-3, while the growth at the roots is limited by diffusion of the segregated solute. The second important part of growth is the propagation of the solid into a new cell, the concept of which is shown schematically in Figure 3-3 for the CA model. In this model, the cell is not necessarily entirely solid before the growth proceeds into the neighbouring cell; this represents the passage of the tips of a network of dendrites through the cell. The parameter f_s^g , the fraction solid at which growth proceeds into a neighbour cell, represents the shape and spacing of the dendrite arms when they are smaller than the cell size.

These approximations are necessary for modelling using cells that are larger than the dendrite arms, otherwise the model in effect forces the dendrite tip to be as wide as one cell, forcing a planar front under conditions where planar growth is not stable, causing an unstable oscillation of the growth rate.

The capture of neighbouring cells requires only a single neighbour cell to be solid. This scheme results in grid-aligned dendrites as shown in Figure 3-4. The use of a decentred square or octahedron method as reported by Gandin [85, 100] could be used to mitigate the grid alignment [86] however, the scale of the cells would need to be small enough to fully resolve the secondary dendrite arms. This would require cells on the order of one micron, thus requiring very small time steps to model the diffusion of gas.

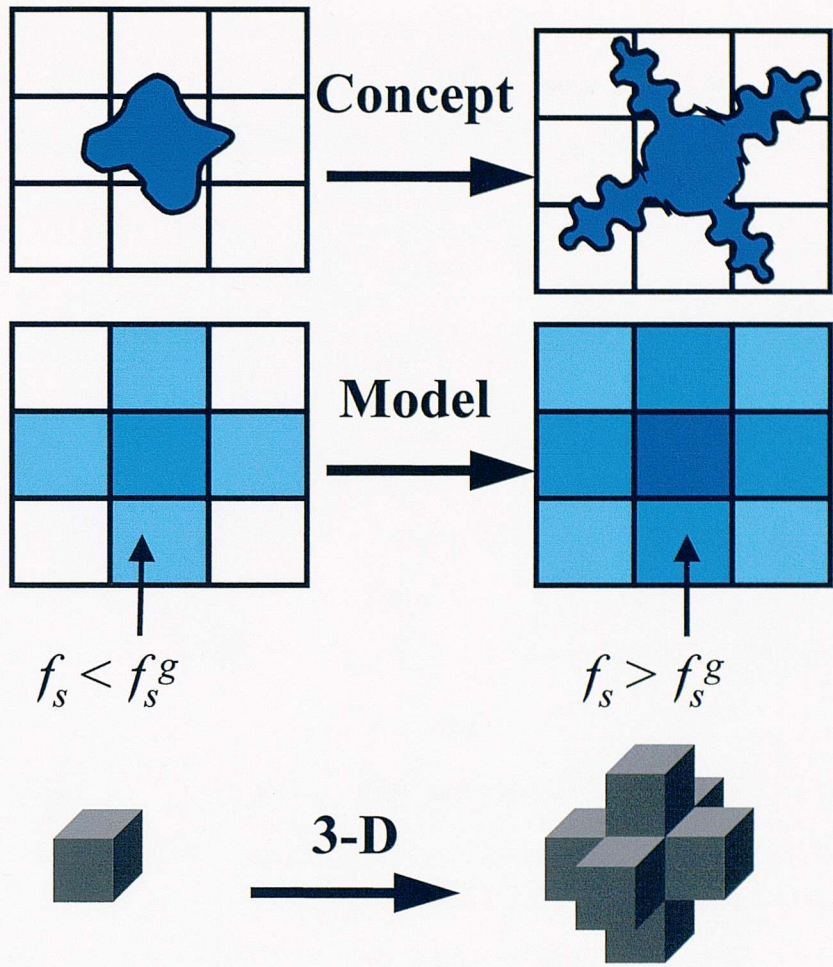


Figure 3-3. Illustration of the cell capture concept. If the cells are understood to contain dendrites which have arm spacing less than the cell dimension, then the cell will not be fully solid when the growth proceeds to the neighbouring cell.



Figure 3-4. Example of the dendrite morphology produced by the solidification model using a 500x500x25 cell domain.

The driving force for both the nucleation and growth schemes is the undercooling, representing the deviation from equilibrium. There were two ways of interpreting this quantity; the deviation of the system as a whole, in which case the undercooling is the quantity ΔT_g :

$$\Delta T_g = T_{liq} - T_c, \quad (3-9)$$

or the deviation from equilibrium of each cell, in which case the undercooling is the local quantity ΔT_l :

$$\Delta T_l = T_{eq} - T_c, \quad (3-10)$$

where T_{liq} is the liquidus temperature of the original alloy composition, and T_{eq} is the equilibrium liquidus temperature for the composition of the liquid in the cell, and T_c is the temperature in the cell. The equilibrium liquidus is given by a linear approximation:

$$T_{eq} = T_{ref} + mC_l \quad (3-11)$$

where T_{ref} and m are chosen to give a suitable linear approximation for the system being modelled. Each of the systems modelled in this study are eutectic systems in the compositional range of interest, so the approximation chosen was a line passing through the eutectic (T_{eut} , C_{eut}) and the equilibrium liquidus point of the original alloy composition (T_{liq} , C^i) and T_{ref} is the intercept of this line with the $C=0$ axis:

$$m = \frac{T_{eut} - T_{liq}}{C_{eut} - C^i}; \quad (3-12)$$

$$T_{ref} = T_{liq} - mC^i.$$

Two versions of the growth model were implemented, referred to as the **Gulliver-Scheil** model and the **phase diagram** model respectively. In the Gulliver-Scheil model, the global undercooling ΔT_g is used to determine the growth rate, whereas in the phase diagram model the local undercooling ΔT_l is used. In the Gulliver-Scheil model, the state of the cell is interpreted as the position of the dendrite envelope, and the actual fraction solid and concentration of dissolved species is determined by the Gulliver-Scheil equation (Equation 2-10).

In the phase diagram model, the local undercooling ΔT_l is used, and the state of the cells is interpreted as the fraction solid of the cell. The KGT model, Equation 3-3, is applied to each

cell as a first approximation of the growth rate. Away from the dendrite tips, the build-up of solute due to nearby cells also solidifying tends to reduce the diffusion of solute away from the cell, violating the assumption of growth into an infinite medium. With a far field concentration equal to C_{init} , the growth rate thus predicted is too great and causes the calculated C_l according to Equation 3-7 to be greater than the equilibrium concentration C_{eq} according to Equation 3-11. Therefore, if the first approximation of the new C_l from Equation 3-7 is greater than C_{eq} , then a further refinement to the calculation is done, essentially one iteration on the concentration, to determine the change in fraction solid f_s^{eq} which would result in a concentration of C_{eq} in the cell:

$$f_s^{eq} = \frac{1}{1-k} - \frac{C_l}{(1-k)C_{eq}} + \frac{f_s C_l}{C_{eq}} \quad (3-13)$$

when the cell was not undergoing eutectic growth.

If the cell temperature is below the eutectic temperature and its concentration is at or above the eutectic concentration, the undercooling is measured with respect to the eutectic temperature. Equation 3-6 was reformulated to include the fraction of eutectic f_e :

$$\frac{\partial}{\partial t}(f_s C_s + f_l C_l + f_e C_e) = \nabla \cdot D_{eff} \nabla C_l. \quad (3-14)$$

By assuming:

- that either primary phase or eutectic phase, but not both, was forming in a single cell; therefore $\frac{\partial}{\partial t} f_s = 0$;
- that the eutectic concentration was constant, therefore $\frac{\partial}{\partial t} C_e = 0$;
- and that diffusion of the solute in the solid within eutectic cells could be neglected, therefore $\frac{\partial}{\partial t} C_s = 0$;

the finite difference form of Equation 3-14 could be written in terms of the concentration and fraction liquid, without tracking the amount of solid and eutectic in each cell:

$$C_l^n = C_e + \frac{f_l^o}{f_l^n} (C_l^o - C_e) + \frac{1}{f_l^n} \Sigma^o \quad (3-15)$$

where Σ^o is the finite difference expression for the flux into the cell, Equation 3-8.

3.2. Pore Nucleation and Growth

The simulation of the formation of the pores was implemented within the developing network of solid, including the processes of nucleation and growth of individual pores and diffusion of dissolved gas. In this model, the shrinkage pressure is not calculated.

Two different techniques were developed for the simulation of the pores. Firstly, a model in which the pores were treated as free growing spheres was developed and applied to situations where this model was appropriate. Secondly, the model was extended by allowing the pores to expand by a CA technique, taking on complex shapes within the simulated solid structure. This model allowed the application of the technique to experimental situations in which the former model was not adequate. The method used for determining the nucleation of the pores was the same in each case. This is described below, followed by details of the pore growth simulation.

3.2.1. Nucleation

The nucleation of pores was determined by a stochastic model similar to that used for the solid; however, the probability depended upon the local hydrogen supersaturation, s , (defined as the ratio of the equilibrium and actual concentrations of hydrogen, $s = C^H / C_{eq}^H$) in the cell. Otherwise the technique of developing the nucleation distribution for the gas phase was the same as for the solid. The step function was defined by the minimum threshold, s_{min} , the maximum threshold, s_{max} , and the total number density of nuclei, n_n . The Gaussian function was characterised by the mean nucleation supersaturation s_c , the deviation of the distribution s_σ and the number density n_n .

If the calculated supersaturation in a cell containing a nucleation site exceeds the threshold for that site, a pore at equilibrium with the hydrogen concentration in that cell is created. The initial radius, r_i , is determined by Equation 3-17 combined with Sieverts' Law:

$$r_i = \frac{2\gamma}{\Pi_a(s^2 - 1)}, \quad (3-16)$$

where γ is the gas-liquid interfacial energy and Π_a is the local (applied) pressure. This mimics a Type IV nucleation process of Jones *et al.* [34] as described in Chapter 2, in that any site produces a bubble with 100% probability once its threshold is reached. The temperature and supersaturation at which each modelled pore nucleated is recorded for subsequent analysis.

3.2.2. Growth of Pores – Spherical

In the spherical pore growth model, the following simplifying assumptions were used:

1. The pores are spherical.
2. Each pore only sinks hydrogen from a single cell.
3. The pores do not move or coalesce.
4. Pore growth is not restricted by the solid.

In each cell containing a pore, at each time step, hydrogen was equilibrated between the pore and the metal. The new radius of the pore, r_p , was then determined from the pressure in the pore Π_p , the volume of the pore V_p and the number of moles of gas, n_{mol} , in the pore and its temperature using the ideal gas law,

$$\Pi_p V_p = n_{mol} \mathbf{R} T \quad (3-17)$$

combined with the effect of the interfacial energy:

$$\Pi_p = (\Pi_a + \frac{2\gamma}{r_p}). \quad (3-18)$$

and the assumption that all pores were spherical, hence:

$$V_p = \frac{4\pi}{3} r_p^3 \quad (3-19)$$

where $\mathbf{R}$ is the ideal gas constant.

Newton's method was used to solve the cubic equation for r_p resulting from the combination of Equations 3-17 -- 3-19,

$$\frac{4\pi}{3} (\Pi_a r_p^3 + 2\gamma r_p^2) = n_{mol} \mathbf{R} T \quad (3-20)$$

The amount of gas to transfer was determined by comparing the solubility of H in the liquid with the cell gas concentration, C_l^H , and transferring the amount which would bring the metal in the cell to equilibrium with the pore. The solubility of hydrogen in liquid aluminium was determined according to the equation of Imabayashi *et al.* [37] combined with the factor accounting for the effect of dissolved alloy elements on the hydrogen solubility according to Dautre [42]:

$$\log S_{atm} = 2.256 - \frac{2392}{T} - 0.0119 C_l^{Si} - 0.0269 C_l^{Cu} + 0.0170 C_l^{Mg} \quad (\text{ml/100g STP}), \quad (3-21)$$

where S_{atm} is the solubility at atmospheric pressure. The solubility in the solid was determined assuming a constant partition coefficient of 0.1 for hydrogen. Sieverts' law was assumed to

apply so that the solubility of H_2 gas at equilibrium with the pore pressure could be determined by:

$$\frac{S}{S_{atm}} = \sqrt{\frac{\Pi_p}{\Pi_{atm}}}; \quad (3-22)$$

where S is the solubility at pressure Π_p , and S_{atm} is given by Equation 3-21.

Since the transfer of gas could go either from the pore to the metal or from the metal to the pore, the pores could undergo Ostwald ripening. However, the change in solubility due to the curvature of the surface itself [101] was neglected since at the size range of interest ($> 5 \mu m$) this effect is small compared to the pressure effect.

3.2.3. Growth of Pores – Complex

In order to overcome the limitations of assumptions 1 and 4 above (that the pores are spherical and lie within one cell) another method was developed to allow the pores to grow into complex shapes. If V_p exceeded the total volume of the cell it was occupying then the pore was allowed to expand into one of the neighbouring cells, by using a cellular automaton rule as follows:

- The cell having the lowest f_s was chosen as the new member cell.
- If more than one cell had the minimal value among the neighbouring cells, then the one of those having the lowest ∇C^H was chosen.
- If more than one cell had both minimal f_s and C^H then a random choice was made among them.

The same grid and Von Neumann neighbourhood was used for the pore growth as for the solidification.

In the absence of any solid, this has the effect of causing the pores to grow roughly spherical, resembling truncated octahedra on the cubical lattice grid, as shown in Figure 3-5.

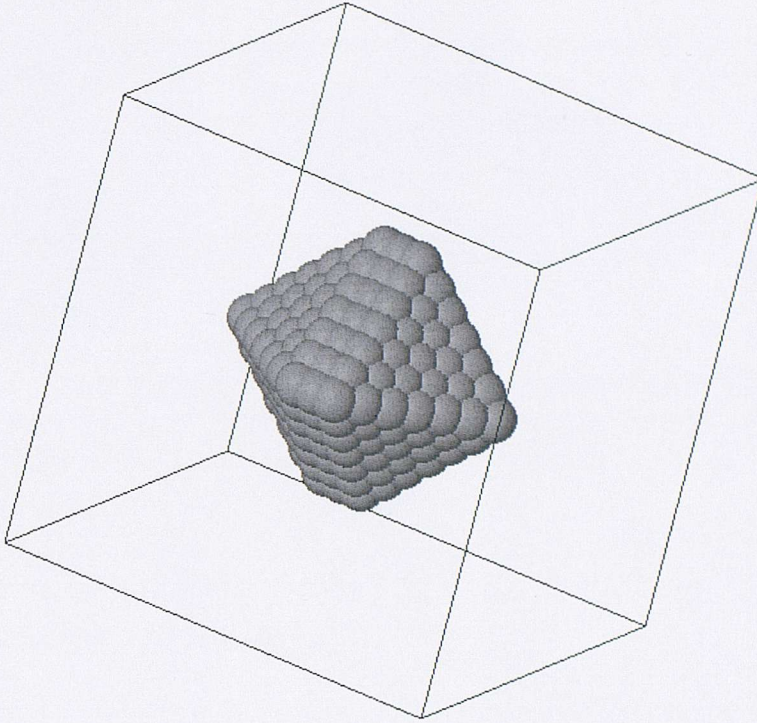


Figure 3-5. A single pore in the centre of a 25x25x25 cell domain takes on a truncated octahedron shape in the CA pore growth model when there is no solid or gradient present.

At the scale at which the model was typically run, the largest pores modelled were typically of order $10^1 - 10^2$ cells in size, so there was little difference between the modelled shape and the grid representation of a sphere.

3.2.4. Growth of Pores – Restricted

The relationship between the pressure, volume, and the amount of gas in a spherical pore is given by Equation 3-20. With a fixed spherical geometry, the pressure and volume can be determined from the amount of gas and the temperature. However, if the pore is not spherical then this relationship no longer holds; and the pressure in the pore is determined by the geometry as well as the temperature. The geometry is determined by the interaction with the surrounding solid phase, which causes the curvature at the pore surface to depart from the spherical curvature. The pressure in the pore, Π_p , is given by:

$$\Pi_p = \Pi_a + \left(\frac{2\gamma}{r_l}\right) \quad (3-23)$$

where r_l is the mean radius of curvature of the liquid-gas interface [102]. The radius of curvature is determined by the shape of the bounding solid and each of the interphase interfacial energies. More generally, the pore adopts a shape such that the overall energy is

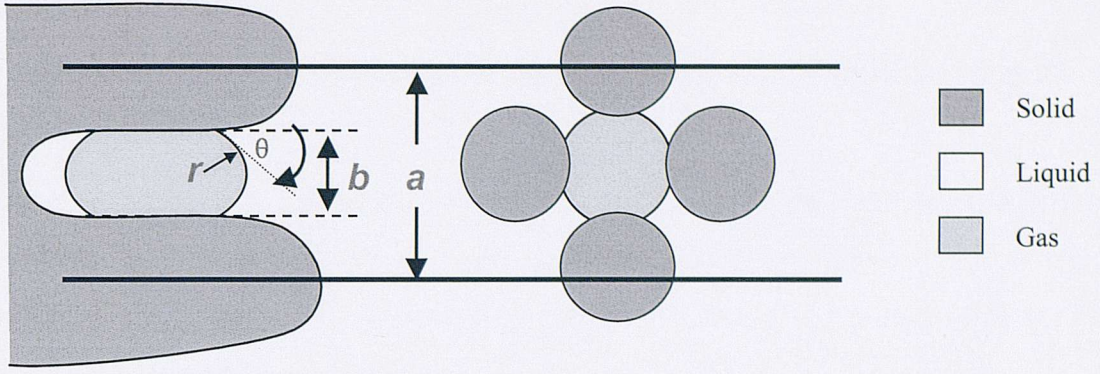


Figure 3-6. Assumption used to determine the pressure and volume of a pore impinging upon the solid. The liquid channel width, b , depends upon the initial spacing, a , and the fraction solid. The radius of curvature, r_l , is assumed to depend upon b and the contact angle, θ .

minimized including the energy due to the compression of the gas within the bubble due to the pressure exerted by the curved interface.

The pores were modelled as bubbles trapped between parallel arms as shown in Figure 3-6. The separation of the surfaces represented the spacing between dendrite arms and was considered to be dependant upon f_s . It was assumed that the capping surface of the bubble was approximately spherical with radius r_l . The radius of curvature for this model could be determined as a function of f_s :

$$r_l = \frac{r_0 (1 - f_s)}{2 \cos \theta} \quad (3-24)$$

where θ is the contact angle between the solid-liquid and gas-liquid interfaces.

However, this model required a further approximation for practical application, since the values of the three interfacial energies were not known. The initial spacing r_0 was assumed to be determined by a power law relationship based on the observed relationship between dendrite arm spacing and the solidification time [4] with the proportionality constant including the contact angle term, thus Equation 3-24 becomes:

$$r_l = (A_\lambda t_s^b)(1 - f_s) \quad (3-25)$$

which required foreknowledge of the solidification time during the modelling of the pore growth. Therefore, this simplification was most appropriate when the situation could be reasonably approximated by constant cooling. It was assumed that although the geometry is somewhat more complex than Figure 3-6, the pressure might follow this relationship approximately, but with some effective initial spacing $r_e = A_\lambda t_s^b$ such that:

$$r_l = r_e(1 - f_s) \quad (3-26)$$

The parameters A_λ and b could then be determined empirically by comparing the model results to experiments.

As the pore grows into the narrowing channel, the gas pressure must increase if the pore volume is to increase, due to the decreased radius of curvature of the gas-liquid interface. At each timestep, the pressure Π_i calculated by assuming V_p remains constant while the amount of gas and the temperature both change,

$$\Pi_i = \frac{n\mathbf{R}T}{V_p}, \quad (3-27)$$

is compared to the pressure exerted according to the above assumption through Equations 3-23, 3-24, and 3-25. If Π_i is less, it is assumed that the pore remains constant in volume and the pressure changes to Π_i . If Π_i is greater, it is assumed that the pore may grow and the new volume is calculated assuming that the pressure is constant at Π_p :

$$V_p = \frac{n\mathbf{R}T}{\Pi_p} \quad (3-28)$$

3.2.5. *Single Bubble Surface Model*

In order to verify the accuracy of the approximation in Equation 3-25, a single bubble model was studied using the Surface Evolver[†] program by Brakke, which has already been used successfully for a variety of problems in metallurgy and other fields [103, 119] (and references therein). This model minimizes the total energy including the surface energies and volume energy due to the compression of an ideal gas. The surface is discretised into triangular elements and a finite element method is applied to find the minimum energy configuration.

The solid-gas boundary could be handled in two different ways. Firstly, by discretising the entire surface and assigning a different energy per unit area to elements of the solid-gas boundary, and secondly, by omitting the solid-gas boundary surface from the discretisation and including the energy and volume due to this surface via boundary integrals.

The first method has the disadvantage of requiring many more elements, and the method of imposing constraints by moving each node by the method of steepest descent and then

[†] Available by download from <http://www.susqu.edu/facstaff/b/brakke/evolver/evolver.html>

projecting back to the defined boundary often caused kinks and degenerate elements, thus slowing convergence, generally requiring that the model be run interactively. The second method was not feasible unless the geometry of the boundary allowed an integrable normal vector field. Therefore this model is not immediately directly applicable to the complex shapes generated by the CA model. However, it is straightforward to apply to the simplified geometry used to develop Equation 3-25 and to determine the equilibrium relationship between the volume and the amount of gas in the pore for various interfacial energy coefficients to understand the degree by which the approximation deviates from ideality. The results of this exercise will be discussed in Chapter 5 along with the complex pore model results.

3.3. Equipment

All simulations were carried out on a *SGI Origin 2000* computer with *R-10000* processors running under the *Irix* operating system. The programs were written in the 'C' programming language, compiled using the *SGI MIPSpro C* compiler, version 7.3.

4. MODEL VERIFICATION AND VALIDATION

In this chapter, the model is validated against known analytic solutions and experimental results. The behaviour of the growth and diffusion model is compared to Gulliver-Scheil and lever rule predictions, and to classic one-dimensional analytical solutions. The behaviour of the solidification model alone is explored, examining the effects of spatial discretisation and time step. The effect of adjusting the model for grain nucleation on the microstructure in isothermal and directional solidification models is explored, and some limitations of the range of feasible application of the model are presented.

The microstructural predictions of the solidification model are compared to examples drawn from the literature and the experimental work done by colleagues at Imperial College showing good correspondence when the nucleation parameters are empirically determined.

The porosity model is verified in isolation using a single pore in a supersaturated liquid to compare the growth rate with the analytical diffusion limited solution. The following chapter discusses the combined grain growth and porosity model.

4.1. Solidification Model

In this section, the behaviour of the solidification model alone is explored. This part of the model includes the nucleation and growth of grains, and diffusion of dissolved solute.

4.1.1. Evolution of Fraction Solid

Simple analytical models for the amount of solid formed may be developed by applying either the lever rule, Equation 3-4, or the Gulliver-Scheil equation, Equation 2-10. Assuming a constant cooling rate, and solving for the fraction solid as a function of temperature yields the following equations:

$$f_s = \frac{C_i - \frac{\Delta T}{m}}{(k-1) \frac{\Delta T}{m}} \quad (4-1)$$

$$f_s = 1 - \left(\frac{\Delta T}{mC_i} \right)^{\left(\frac{1}{k-1} \right)} \quad (4-2)$$

where ΔT is the compositional contribution to the undercooling, that is, the difference between the melting point of the pure material and the equilibrium liquidus temperature. These represent the extreme values predicted by assuming either complete diffusion in the solid phase or no diffusion in the solid phase; but the effect of concentration gradients in the

liquid and of undercooling required to initiate nucleation are not included. These assumptions are most applicable to the model if a slow cooling rate is applied to an isothermal domain.

The evolution of fraction solid as a function of temperature in an example isothermal solidification model is shown in Figure 4-1, for three conditions: (i) Constant cooling at $1.5\text{ }^{\circ}\text{Cs}^{-1}$ and nucleation undercooling $\Delta T_n = 5^{\circ}\text{C}$; (ii) Constant cooling at $1.5\text{ }^{\circ}\text{Cs}^{-1}$ and $\Delta T_n = 0^{\circ}\text{C}$; and (iii) Constant cooling at $0.01\text{ }^{\circ}\text{Cs}^{-1}$ and $\Delta T_n = 0^{\circ}\text{C}$. In each case there is undercooling below what is predicted by either equation, and as the temperature decreases the f_s rises to the region between the two predictions, as expected. When there is no nucleation and as the cooling rate decreases, the initial solidification approaches the equilibrium liquidus as seen in the expanded scale graph, Figure 4-1(b).

In order to compare similar results for the model during directional solidification, the fraction solid at each isothermal section was averaged and the results plotted against temperature. Figure 4-2 shows the results for (a) fast (0.5 mm/s) and (b) slow (0.1 mm/s) growth models. The results differ from the Gulliver-Scheil and lever-rule predicted values, because the assumption of no concentration gradient in the liquid is no longer approximately valid.

The initial solidification is occurring at a measurable undercooling but the fraction solid rapidly rises to the region between the predictions, illustrating that the approximation is still valid away from the dendrite tips. The pattern of fraction solid evolution is reflected in the profile of averaged fraction solid along the length of the domain. Such profiles are shown in Figure 4-3 at (i) 6, (ii) 10 and (iii) 20 seconds, along with the Gulliver-Scheil and lever rule limits for each time. The difference between the model and both Gulliver-Scheil and lever rule predictions at the leading edge of the growth (low f_s) results from the compositional layer building up ahead of the interface, violating the assumption of complete mixing in the liquid., combined with the undercooling required for both the nucleation and growth processes to occur.

The degree of undercooling differs, with the fast imposed velocity resulting in a greater undercooling. This affects the balance between the nucleation and growth processes, favouring nucleation when the imposed velocity is fast. Figure 4-4 shows the resulting microstructures; the fast case (a) results in an equiaxed microstructure whereas the slow case (b) results in a columnar microstructure, in correspondence with the behaviour of the real system. These examples used parameters for Al 1% Si, with a temperature gradient of $6300\text{ }^{\circ}\text{C/m}$.

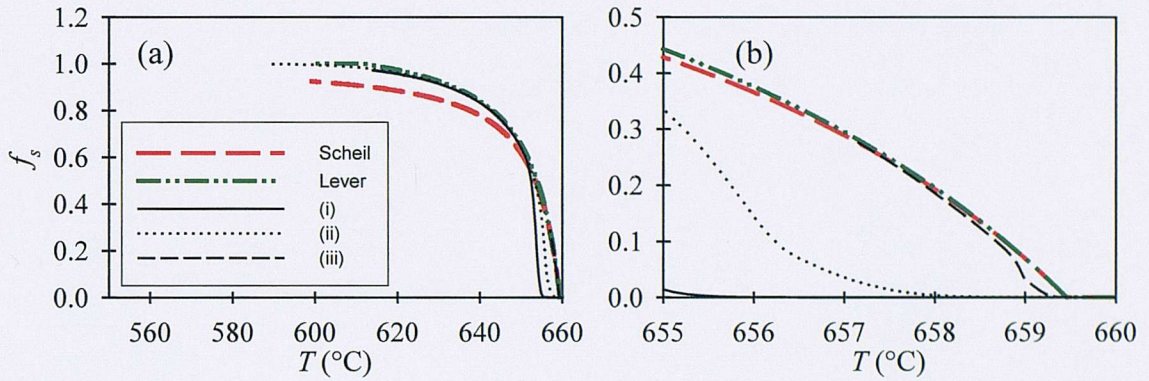


Figure 4-1. (a) The evolution of the fraction solid during isothermal constant cooling compared with predictions of the Gulliver-Scheil equation and the lever rule. (i) Cooling rate $1.5\text{ }^{\circ}\text{Cs}^{-1}$, $\Delta T_n = 5\text{ }^{\circ}\text{C}$ (ii) Cooling rate $1.5\text{ }^{\circ}\text{Cs}^{-1}$, $\Delta T_n = 0\text{ }^{\circ}\text{C}$ (iii) Cooling rate $0.01\text{ }^{\circ}\text{Cs}^{-1}$, $\Delta T_n = 0\text{ }^{\circ}\text{C}$. (b) The same results at expanded scale.

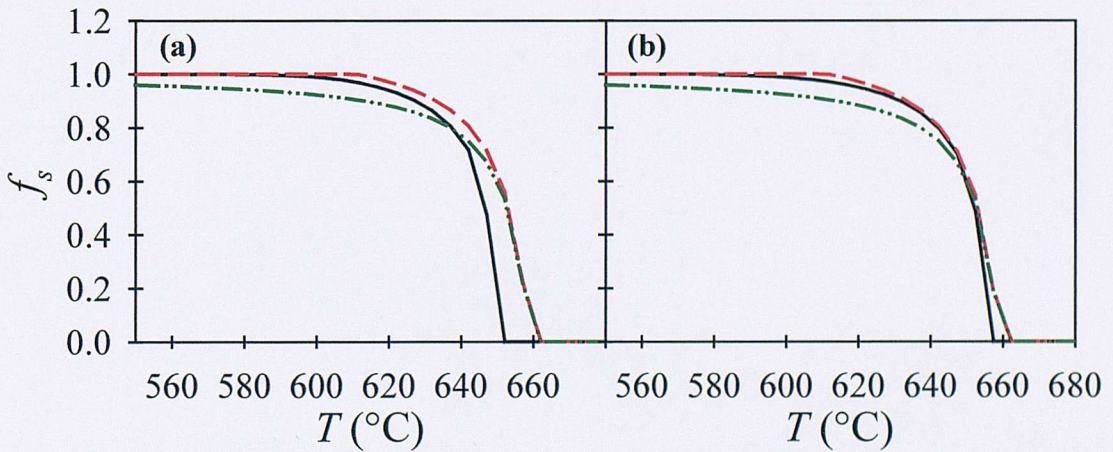


Figure 4-2 The evolution of average fraction solid during directional solidification compared with predictions of the Gulliver-Scheil equation and the lever rule for (a) $V=0.5\text{ mm/s}$ (b) $V=0.1\text{ mm/s}$.

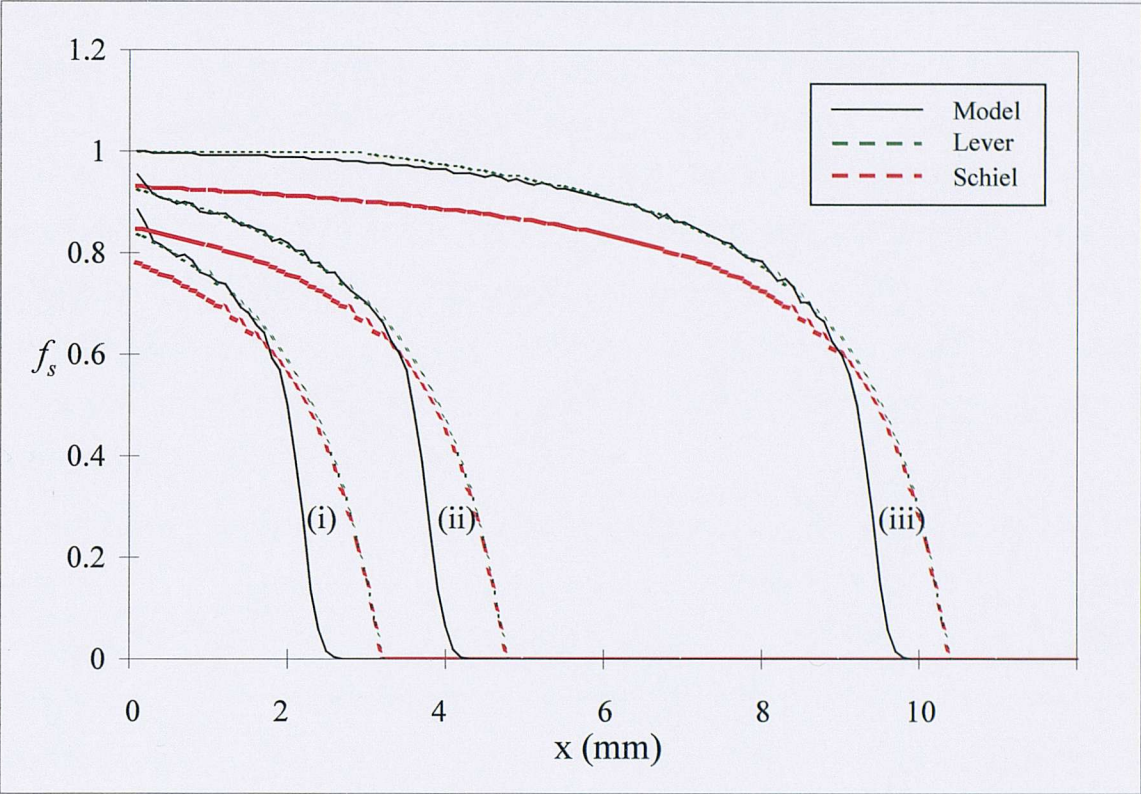


Figure 4-3. Profiles of averaged fraction solid along the length of the model domain compared with the Gulliver-Scheil and lever rule predicted limits, (i) at 6 seconds (ii) at 10 seconds, and (iii) at 20 seconds after the start of solidification.

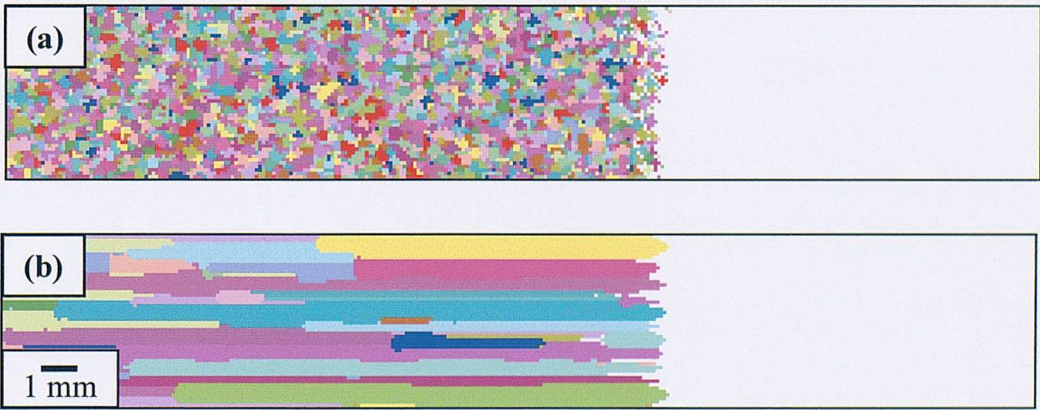


Figure 4-4. The microstructure resulting from (a) fast and (b) slow V using parameters for Al 1% Si.

4.1.2. Directional Solidification in One dimension

The analytical model of Tiller *et al.* [12] includes the concentration gradient ahead of the solidification front in a one-dimensional domain. To reproduce this situation, the model domain was set to a single cell in the directions perpendicular to the growth direction. The distribution of solute in the solid after the directional solidification of this one-dimensional model domain compares quite well to the distribution predicted by Tiller *et al.* [12], Equation 2-11, if the averaged resulting growth velocity is used for R in the equation. The curves are compared in Figure 4-5. For this comparison the diffusivity in the solid was set to zero and in the liquid to $1 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. The Tiller equation assumes that the growth rate is constant; however the growth rate in the model depends upon the undercooling, which in turn depends upon the concentration, so this is not true until steady-state is reached. However, the deviation is only very slight at the start of growth.

The solidification interface in the one-cell-thick model is forced to be planar. Unless the growth rate is very low, the coupling between the solute buildup and the growth rate results in an oscillatory behaviour before the steady state predicted by Tiller *et al.* is reached, as shown in Figure 4-6. This happens because this constrained system is unable to respond to the instability resulting from constitutional supercooling, which should cause the interface to break down into a cellular pattern. Since the spatial instability is impossible, the system responds by developing a temporal instability instead. Even if the model is expanded to a three-dimensional domain, this remains a problem if the growth cell size or dendrite spacing should be smaller than the size of the cells used in the model.

If the growth fraction f_s^g is lowered from unity, allowing microsegregation on a sub cell scale, then the oscillation is reduced, as in Figure 4-7.

The presence of grain nucleation, and the possibility of breakdown of the planar interface into a cellular, dendritic or multigranular pattern when the domain is three-dimensional smooths out the behaviour of the model, resulting in a profile like that in Figure 4-8 in which the domain was $300 \times 20 \times 20$ cells.

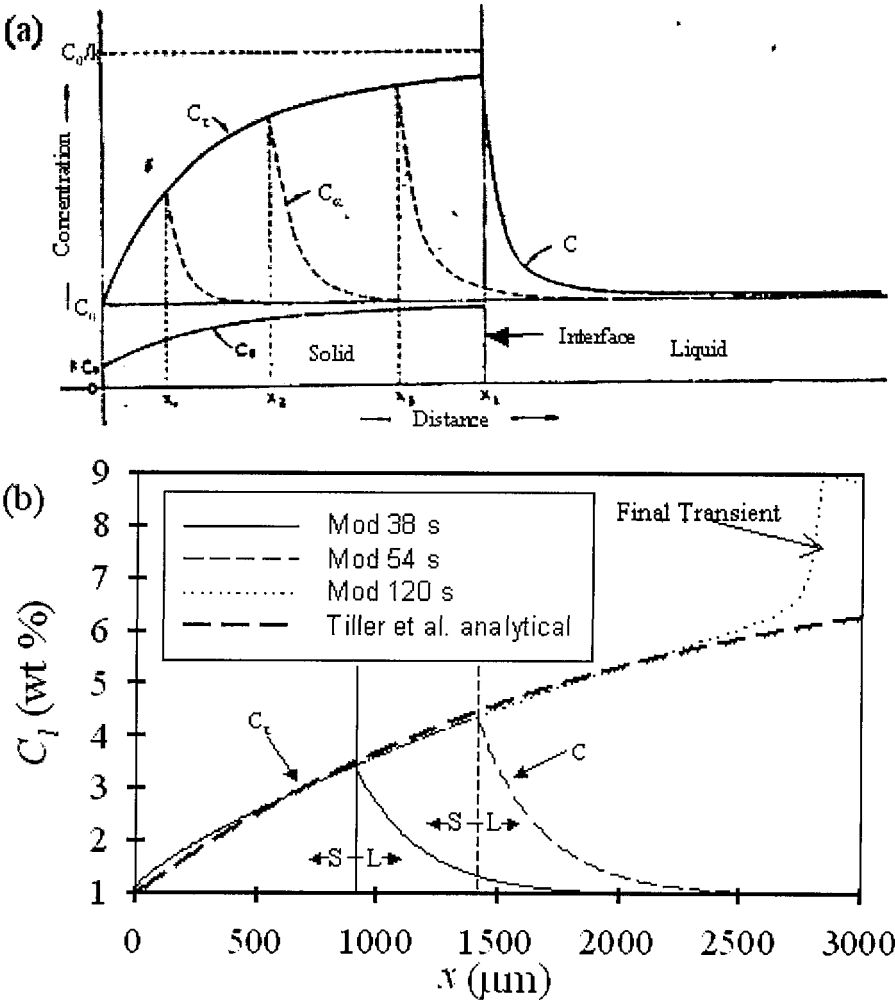


Figure 4-5. (a) The analytical solution of Tiller *et al.* indicating the rise of the interface composition C_t as solidification proceeds, and the compositional layer in the profile of the composition in the liquid, C_l . (b) Comparison between the CA model results for a one-dimensional domain and the analytical result of Tiller *et al.* for C_t (After Tiller *et al.* [12]).

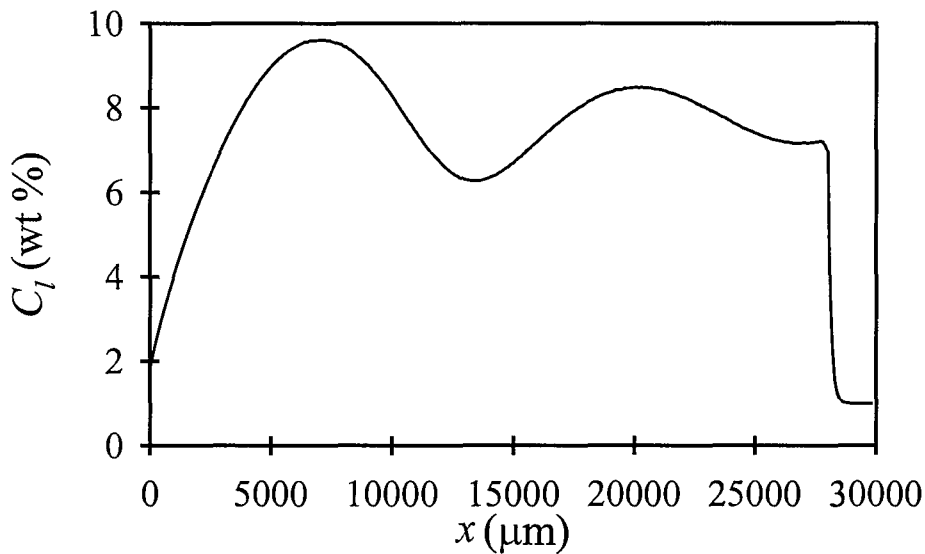


Figure 4-6. Oscillation of the concentration during one-dimensional directional solidification.

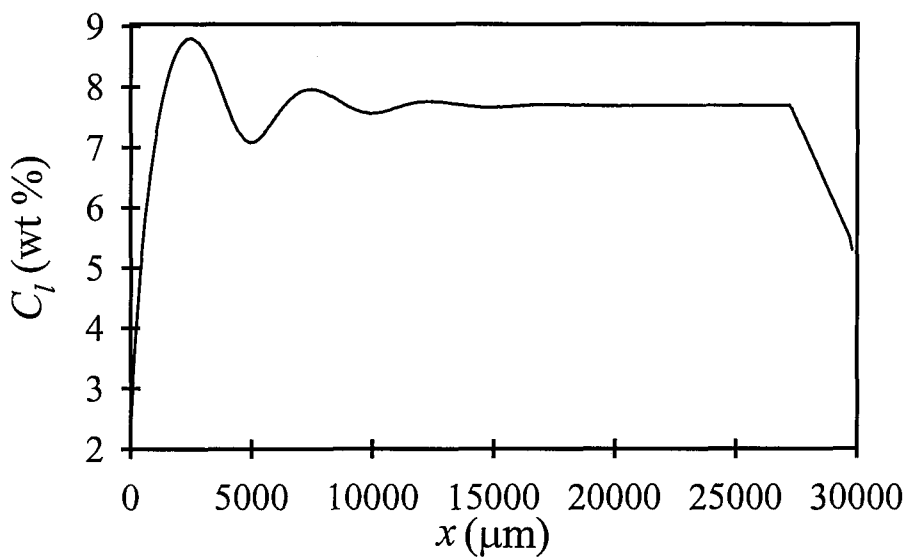


Figure 4-7. Concentration profile resulting when f_s^g is 0.75 during one-dimensional directional solidification.

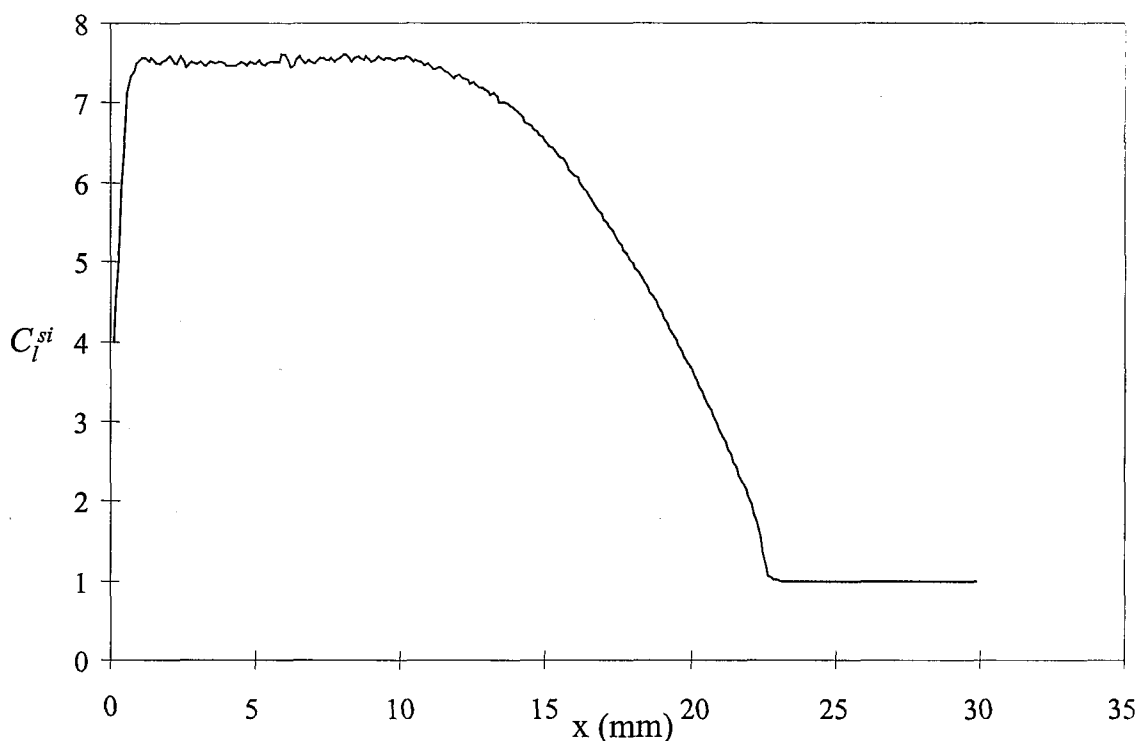


Figure 4-8. Concentration profile resulting for a three-dimensional domain with grain nucleation allowed during directional solidification, averaged across each isothermal slice.

4.1.3. Predicted Cooling Curve.

The model of Charbon and Rappaz was able to successfully predict the recalescence of eutectic cast iron using a similar technique [81]. If the diffusion model is not used, and the latent heat release is calculated from the change in f_s , the current model reproduces these same results. The main difference from their model is that the cellular algorithm is local in this model, whereas the algorithm of Charbon and Rappaz was not; that is, the liquid-to-solid transition depended upon whether a cell lay within a calculated radius of a growing spherical grain. In an isothermal domain, and without diffusion, these differing assumptions lead to the same results, as seen in Figure 4-9. The parameters used duplicate those given in [81].

4.1.4. No Diffusion

The basic form of the solidification model without including solute diffusion and assuming a constant liquidus temperature was tested for sensitivity to the basic modelling parameters of grid cell size and time step to ensure that the model approaches a steady result as it is refined.

Effect of Grid Size

If the size of the cells dx on the grid is reduced, while maintaining the total size of the model domain or number of cells constant, then the resulting grain size converges on a stable value, as shown in Figure 4-10. The grain size is characterized by the average equivalent grain

radius R_a , the average line intercept size in a slice through the model domain L_g , and the number density of grains N_g . Of these, L_g shows the largest scatter; whereas R_a is stable with respect to dx over the whole range, and does not illustrate the reduction in error as the grid is refined. The convergence is most apparent in the behaviour of N_g with decreasing dx ; below about 200 microns there is no significant change.

The limit on large cells is determined by the nucleation model, which does not allow more than one nucleus per cell; by the concept of the model a cell cannot have parts of more than one grain within it as each cell is considered to be a uniform region.

The limit on small cells is determined by the feasibility of implementing the model with run-time and memory limits, and for a constant time-step, by the maximum allowable growth rate. The same nucleation density N_n therefore can not be used for the entire range of cell size; at the small size range a feasible domain would include only one grain whereas at the large size range one cell would need to include multiple grains.

Effect of Time Step

If the time step is increased for a constant grid size, the resulting grain size is constant, so long as the amount of growth in one timestep is significantly less than one cell. Since the CA capture model allows liquid cells neighbouring upon fully solid cells to begin solidifying, the growth front cannot extend more than one cell and the velocity is artificially reduced if this limit is exceeded.

So long as this limit is not approached, the grain nucleation and growth model is insensitive to the time step. In practice, other limitations on the timestep, especially that for the diffusion of hydrogen dissolved in the liquid, are usually more restrictive than this limit and so it is not usually approached.

However, in order to determine the proximity to this limit, the model records the number of instances in which the change in fraction solid in a cell would result in new solid exceeding 0.8 of a cell. The graph in Figure 4-12 shows the average equivalent grain radius, line intercept grain size, and grain number results for a range of time steps with the number of such overgrowth errors superimposed, and Figure 4-13 shows the resulting simulated microstructures. When these errors occur, there is an excess of nucleation resulting from undercooled cells which should have been captured by neighbouring solid. Even at this limit, the effect on the size of the grains is not great, but the effect on the total number of grains is much greater, as shown in Figure 4-12.

For the cases in which overgrowth does not occur, there is some variation. This is due to the stochastic nucleation process, and by repeating each model four times with different random number seed values, the expected variation due to this process is determined. A one-way ANOVA using these values demonstrates that for the responses considered the variation between t_s levels is not significant and can be explained by the variation within each t_s level. The results are shown in Appendix B.

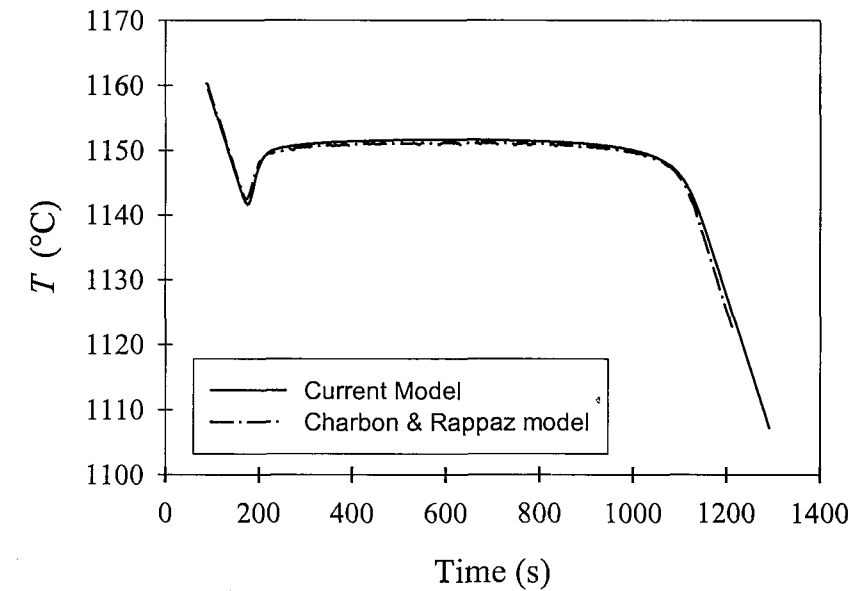


Figure 4-9 A comparison between the model results and the results of Charbon and Rappaz [81] for eutectic cast iron, using their input parameters.

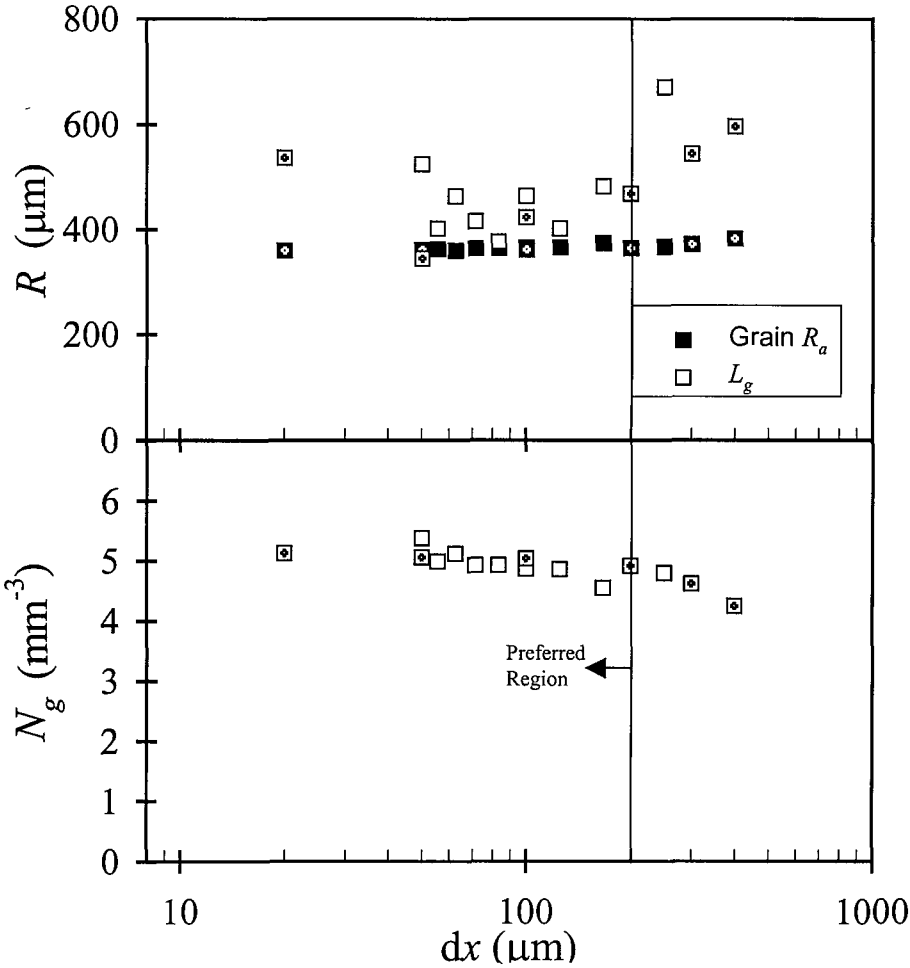


Figure 4-10. The effect of changing the grid cell size on the grain density, average equivalent grain radius and line intercept size. Dotted symbols represent results obtained by maintaining the domain size constant, and undotted symbols represent those obtained by maintaining the number of cells constant.

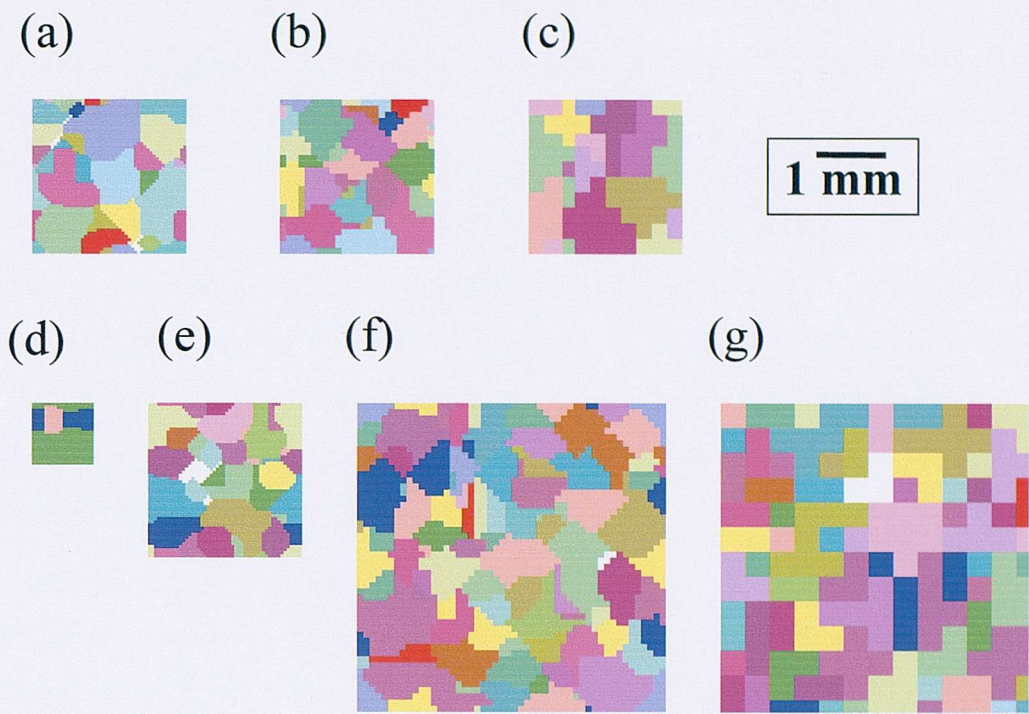


Figure 4-11. Simulated microstructures obtained at different grid sizes shown at a uniform scale. Examples (a), (b), and (c) use equal size cubic domains of 2.5 mm edge, and examples (d), (e), (f), and (g) use domains of 50 cells. The cell sizes are: (a) 50, (b) 100, (c) 250, (d) 20, (e) 50, (f) 100, and (g) 400 μm .

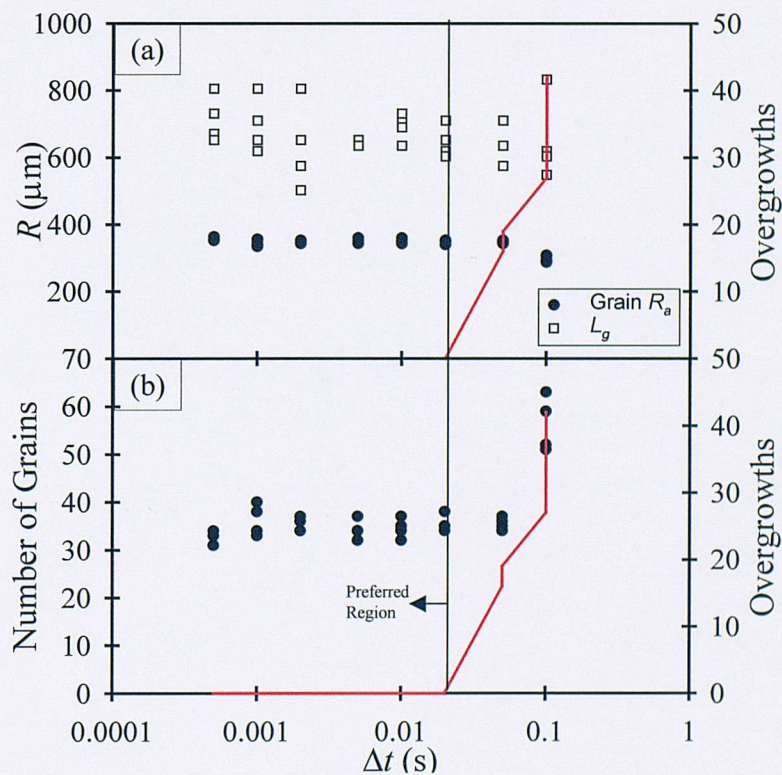


Figure 4-12. Convergence of the grain characteristics as the time step is reduced, compared with the diagnostics indicating growth exceeding 0.8 cells per timestep.

For small time steps, the natural limit of the model is determined by the precision with which the information for each cell is stored. If the amount of change in fraction solid for one time step is less than about 10^{-8} for single precision storage, or 10^{-17} for double precision storage, the difference for cells in which the fraction solid is near unity will not be accurately represented. However, using double precision for all quantities doubles the storage required, so this choice depends upon the number of cells in the domain. Likewise, if the temperature change in one timestep is similarly small, the change in temperature will not be registered and the simulation may never solidify. If one uses reduced precision in order to create a larger (or more finely discretised) model, one must then ensure that the expected changes in fraction solid and temperature are not too small to represent.

4.1.5. *Alloying Element Diffusion*

Once the diffusion of an alloying element is included, the response becomes somewhat more complicated. The limit for the growth model to be insensitive to the grid size depends upon the characteristic length scale of the diffusion and this generally is more restrictive in the situations of interest than is the growth limit described above

Grid size with diffusion

At the scale appropriate for modelling the population of pores, the cell size is generally larger than the secondary dendrite arm spacing. Therefore the growth rate is artificially slowed when the cell size is large. The model requires that f_s in the cell reach unity before neighbouring cells can begin to solidify; so it behaves as a dendrite which is artificially constrained to have a width of dx . The dendrite arm spacing cannot then be less than $2dx$ or the interface is forced to be planar, and the growth rate is artificially slowed. This results in smaller final grain size if the grid cells are larger, as seen in Figure 4-14(a) for three different cell size meshes of the same model domain. Figure 4-14(b) shows the slices when partly solidified, showing finer dendrite structure in the finer mesh which allows faster diffusion-limited growth.

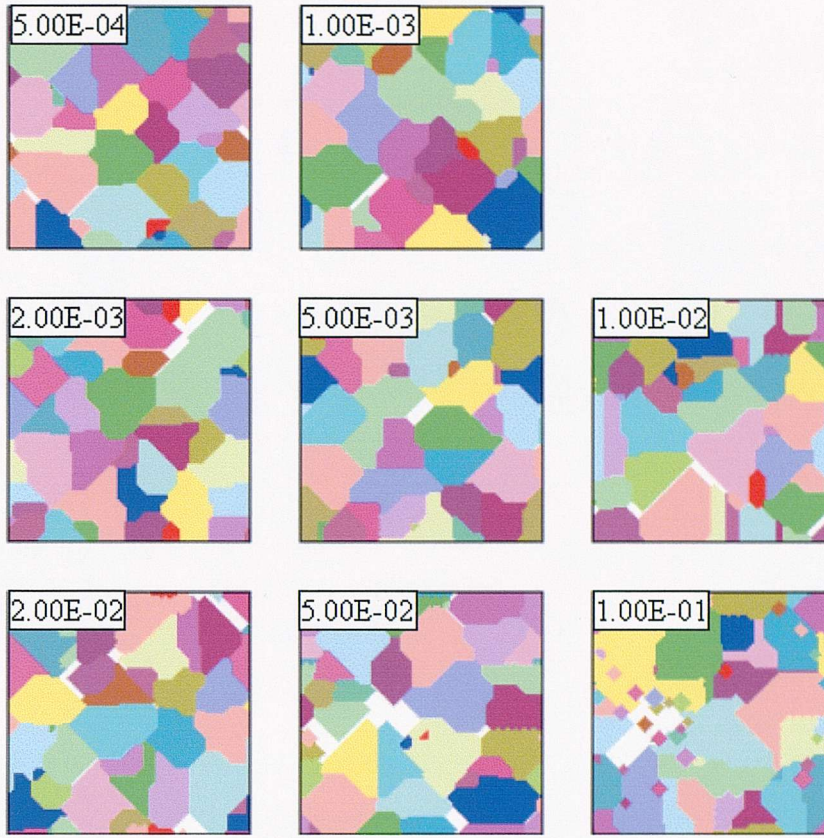


Figure 4-13. Simulated microstructures produced at a variety of values of the timestep Δt using the basic CA solidification model. There is no discernable effect if the predicted growth rate does not extend the solid by more than one cell per time step.

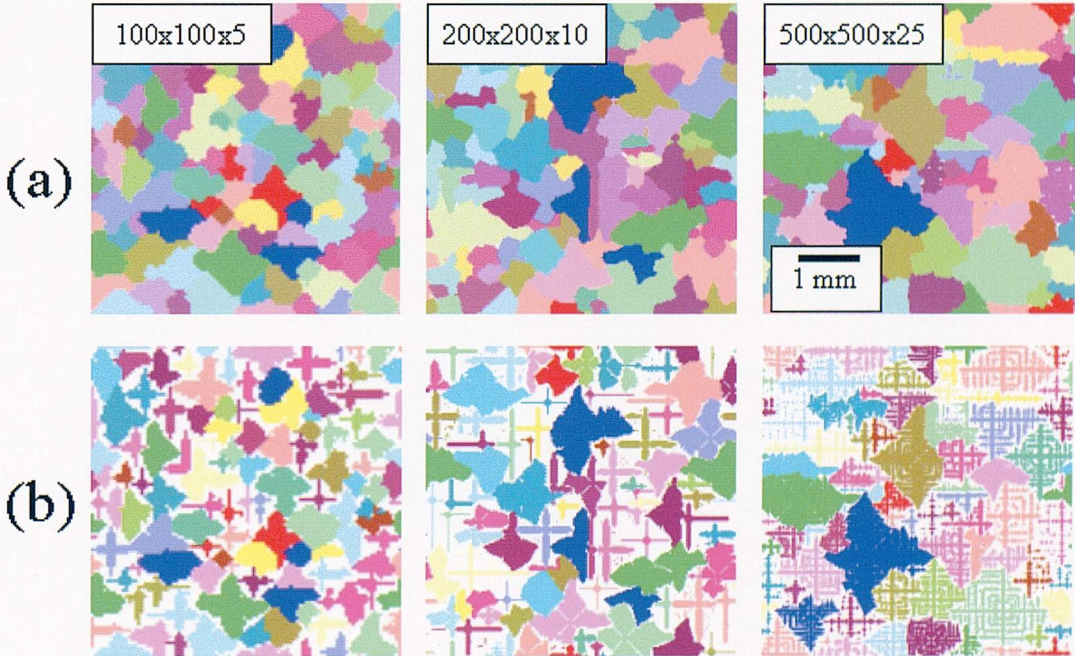


Figure 4-14. Three models of the same region at different mesh size, maintaining f_s^g , showing some dependence upon the grid size. (a) The final microstructure. (b) The structure when partly solidified.

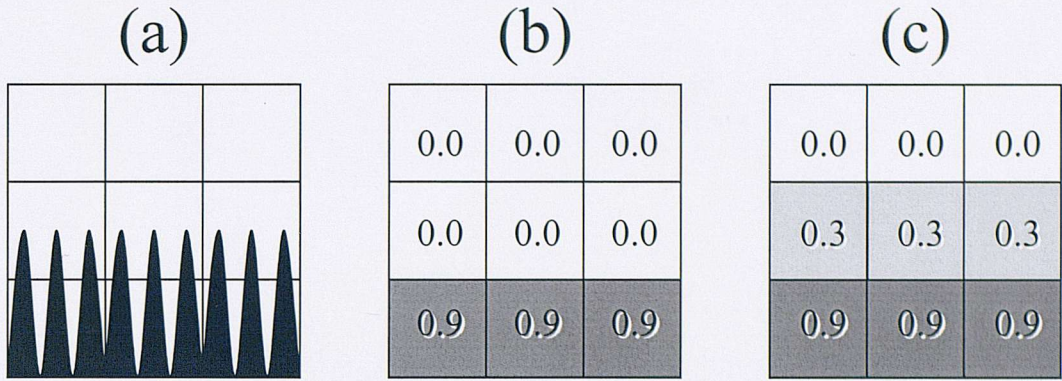


Figure 4-15. Illustration of the need for the constant f_s^g . If the fraction solid must be unity for growth to proceed, the simulated solid does not grow as fast as it should, if the dendrite spacing is smaller than the cell size. A schematic of a dendritic front with the discretisation is shown in (a), and the cellular representation assuming that growth may only proceed if f_s must be unity is shown in (b) along with the f_s for each cell. In (c) the result of allowing growth to proceed when f_s is 0.8 is shown, (c) is a better approximation to (a) than (b) is.

This problem is ameliorated by introducing the growth factor f_s^g ; a constant less than unity representing the fraction solid at which growth proceeds into a neighbouring cell. Figure 4-15 illustrates the concept. If a cell contains dendrites with a spacing smaller than dx , then the cell is not fully solid when growth proceeds to the next cell. Reducing the fraction solid required for growth to proceed in the model then simulates this behaviour. This is illustrated schematically in Figure 4-15. If a dendritic front is discretised upon cells which are larger than the dendrite arm spacing, as in (a), the fraction solid in the bottom row of cells would be less than unity, whereas the fraction solid in the middle row would be greater than zero. Requiring f_s to be unity before growth may proceed results in the situation (b), in which no solid is formed in the middle row. If growth may proceed at a smaller value of f_s , then the situation in (c) results, which is better approximates (a) than does (b). The f_s^g represents the threshold value of f_s at which growth may proceed into neighbouring cells.

Figure 4-16 shows the dependence of the grain size, indicated by the average spherical radius R_{av} , on the combined factors of cell size and f_s^g illustrating how the f_s^g can compensate for this effect of grid size.

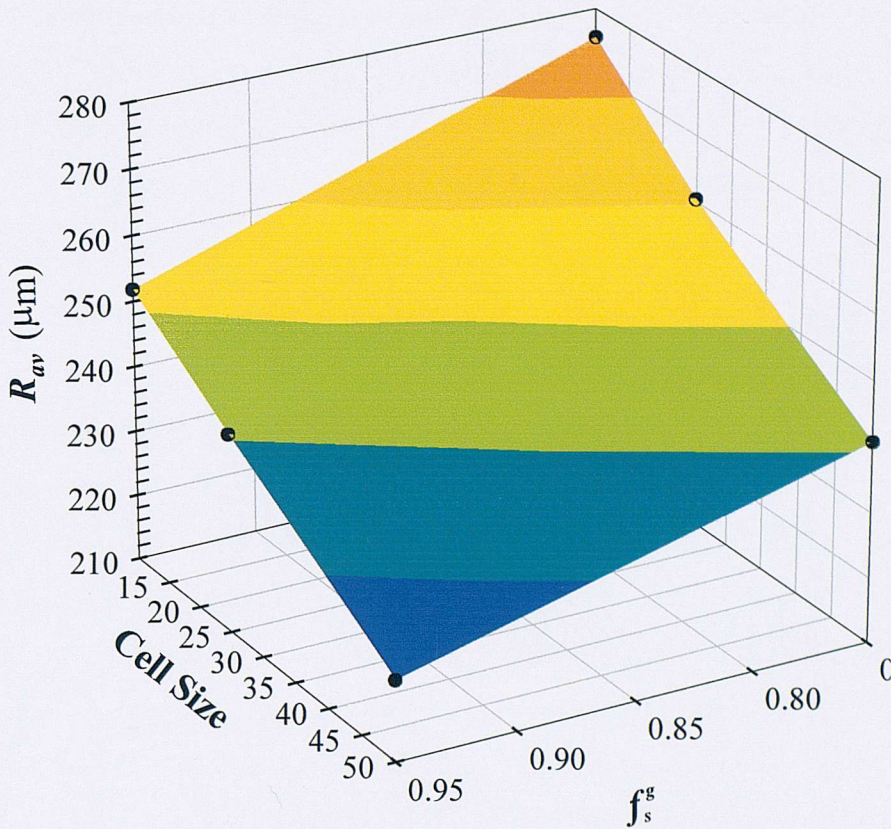


Figure 4-16. Grain size results when the grid size and f_s^g are both varied.

4.1.6. Limits

The limits on the choice of model parameters result from a number of restrictions, due to stability, resolution, and practical use. The limits discussed above in connection with grid size and time step choice may be combined with numerical stability, resolution, and practical limits in a graphical representation, as follows.

The best-case limit for the stability of the diffusion solution is given by the Courant stability criterion [104] applied to the three-dimensional finite difference scheme, for which the criterion is:

$$\frac{D\Delta t}{\Delta x^2} < \frac{1}{6} \quad (4-3)$$

This criterion is plotted as a line on a log-log plot of Δt vs. Δx in Figure 4-17, as line **a** for silicon and **b** for hydrogen. Only the diffusivities in the liquid are included, as these are always greater than those in the solid and result in more restrictive limits. The arrows point toward the side of the line which satisfies the inequality in Equation 4-3.

The maximum Δx to represent the diffusion layer may be estimated from the magnitude of D/v , by assuming a maximum expected undercooling ΔT_{max} and determining v using Equation 3-3. Of course, the exact undercooling is not known prior to running the model, but it can be estimated based upon knowledge of the real application for which the model is to be used. The lines representing the limits for an assumed δT_{max} of 5°C are plotted in Figure 4-17 as **c** for silicon and **d** for hydrogen.

The numerical resolution of the calculations also imposes limits. In order to accurately calculate the temperature, the temperature drop in one time step must not be below the chosen resolution for the storage of the temperature value. Likewise, the change in fraction solid in a cell during one timestep should not be below this level. The limit imposed by the former requirement depends upon the chosen numerical resolution and the cooling rate, and is represented by line **e**. The limit imposed by the latter depends upon the growth rate, which depends upon the minimum undercooling δT_{min} for which the model should register growth and the growth law used in addition to the numerical resolution chosen. This limit is represented by line **f**.

Furthermore, the chosen cell size Δx should be able to represent the expected grain structure. This limit is indicated by line **g**. If the growth rate is quite large, it is possible that the growth rule dictates that the interface should move by a distance greater than one cell, which the CA growth mechanism cannot represent. Choosing an ‘error limit’ of 0.8 of one cell per timestep, and estimating the maximum undercooling δT_{max} gives a limit represented by line **h**.

Practical limits are imposed by the amount of time that the calculation will take and the amount of computer memory available. The time may be estimated for any combination of Δx and Δt given the total volume V_{tot} of the domain and τ , the time to calculate one cell for one step using a particular computer. This results in the limit represented by line **i**. Similarly, from V_{tot} and the Δx , the storage necessary may be estimated from the storage required for each cell (which also depends upon the resolution chosen for the calculations). This results in the limit represented by line **j**.

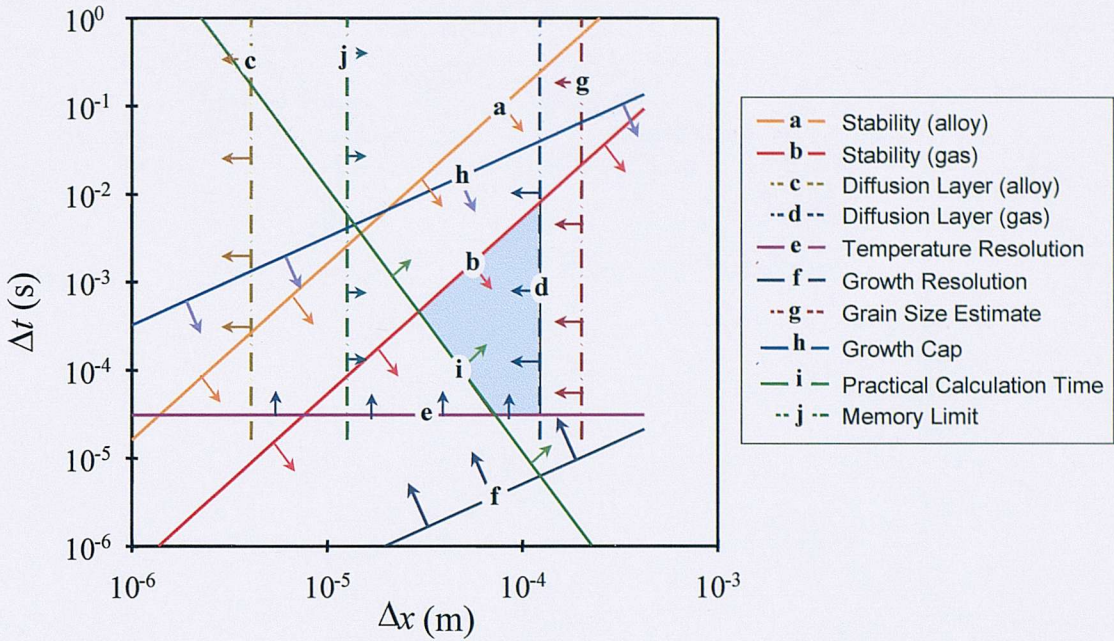


Figure 4-17. Estimated limits of discretisation for accuracy and stability of the model, assuming the parameters given in Table III.

Combining these limits to the accurate and practical use of the model results in the diagram in Figure 4-17 using the parameter values in Table III. The arrows indicate on which side of each line the limit requires the model to lie. The target volume was chosen as suitable for representing a sample of 10 pores if the pores have a number density of 1 mm^{-3} (10^9 m^{-3}). This particular chart depends upon the values used in Table III, and different versions of this chart would result from other choices of parameters suitable to the problem under consideration, or a different computer.

For the example in Figure 4-17, the fixed cooling rate of $1.5 \text{ }^\circ\text{C/sec}$ determines a lower limit of order 10^{-5} seconds with single precision arithmetic, in order for the temperature change to be calculated. Double precision arithmetic changes this to about 10^{-17} s at the expense of increased memory use. Line **e** represents the single precision limit for temperature; in this case it borders upon the shaded region of interest, and hence could represent the first limit to have an effect if the time step is reduced, especially if a longer choice of the practical time (or a faster computer) shifts line **i** to the lower left exposing more of line **e** to the region of interest.

Table III Values used for Limits in Figure 4-17

<i>Quantity</i>	<i>Value</i>	<i>Units</i>
D_l^{Si}	1.00×10^{-8}	$\text{m}^2 \text{s}^{-1}$
D_l^{H}	3.00×10^{-7}	$\text{m}^2 \text{s}^{-1}$
Growth Cap	0.8	cell
Cooling Rate	1	$^{\circ}\text{C s}^{-1}$
T_i	617	$^{\circ}\text{C}$
α_g	9.85×10^{-5}	
$\delta T_{\min}$	0.1	$^{\circ}\text{C}$
$\delta T_{\max}$	5	$^{\circ}\text{C}$
Precision	5.00×10^{-8}	
Stability	1.60×10^{-1}	
τ	1.00×10^{-6}	sec/cell. step
V_{tot}	1.00×10^{-8}	m^3
T_{tot}	100	s
Time Limit	86400	s
(Equiv. Time Limit)	1	day
Memory Limit	1.00×10^9	bytes
Storage	200	bytes/cell

Of particular interest is the region bounded by **b**, **d** and **i** which represents the region in which a stable calculation of the gas diffusion may be performed in one day, with sufficient resolution to model the diffusion layer of gas ahead of an advancing solid interface, for the chosen 1 mm^3 volume. The intersection of **b** and **c** represents the parameters suitable for stable calculation of the gas diffusion, with sufficient spatial resolution to model the diffusion layer of solute ahead of the advancing solid interface, however this region lies quite far to the right of **i**, indicating long calculation times. The apex of this region, representing the marginally stable calculation with the minimum resolution, lies approximately on the 1000-day line for estimated calculation time. This analysis shows that it is not feasible to model the diffusion layer and hence the secondary dendrite structure at the same time as the gas pores in this straightforward fashion. This underscores the need for an approximation using f_s^g as described above, in order to model at the desired mesoscopic scale for the representation of gas porosity.

4.1.7. Response to Nucleation Parameters

The results of several simulations, varying the nucleation parameters T_n , N_n and T_s at different cooling rates and for the three nucleation models (0—step, 1—quadratic, 2—Gaussian) were analysed to determine the relative effects of each parameter on the grain size. The results determined from the array of experiments using the parameters in Table IV are shown in Figure 4-18, which shows the contrast, or effect on the average due to each factor level after factoring out the effects of the other factors. The statistical analysis is presented in Appendix B. Five levels (a, b, c, d, e) of the nucleation parameters were used for each of two cooling rates and three nucleation models; a central-composite type of experimental design was used, limiting the number of runs to eighteen per combination of cooling rate and nucleation model. The points chosen in this layout may be represented as the corners of a cube in a three-dimensional space, plus additional points centred on the faces and at the centre of the cube as described in standard references on experimental design [105-107].

Table IV. Levels used for the grain nucleation response tests.

Parameter	a	b	c	d	e
T_c (°C)	5	7	10	13	15
N_n (m ⁻³)	1.00E+09	2.50E+09	1.00E+10	3.90E+10	1.00E+11
T_σ (°C)	1	1.8	3	4.2	5
Cooling Rate (°C/s)	0.1	0.5			

The main effect on grain size is due to the number of potential nuclei, N_n , which has a dominant effect at all cooling rates. At the high cooling rate, the effect of the T_c and σ are insignificant. At low cooling rate there is some effect due to these parameters, as shown in Figure 4-18. The effects can be isolated statistically; an analysis of variance (ANOVA) for the four factors (N_n , T_c , σ , Nucleation Model) using the data at low (0.1 °C/s) and high (0.5 °C/s) cooling rates shows that all the factors have statistically significant effects on the grain R_{av} at the low cooling rate, and the significance of all but T_c is reduced at the high cooling rate, the nucleation model type becoming insignificant. See Appendix B for the analysis. The magnitudes of the contrasts are compared graphically in Figure 4-18; the effect of N_n dominates but the other factors T_c and T_σ are noticeable at the low cooling rate.

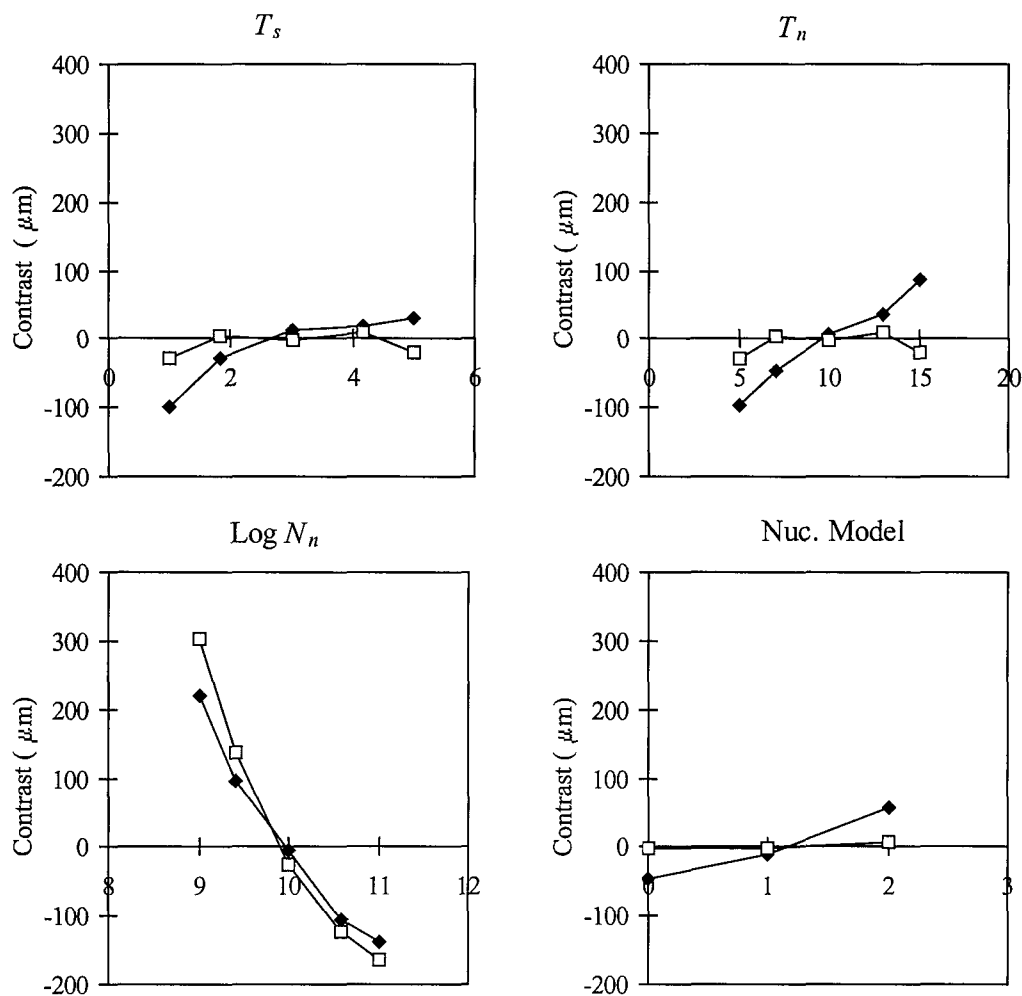


Figure 4-18. Graphs of the contrasts isolated by the analysis of a series of experiments varying T_s , T_n , N_n , and the nucleation model, showing the effect of varying the nucleation parameters upon the average grain equivalent radius at high (hollow symbol) and low (solid symbol) cooling rate.

At the high cooling rate, the nucleation models predict effectively instantaneous nucleation; whereas at the lower cooling rate, the nucleation sites interact more. Consider a nucleation site S_1 with a threshold undercooling T_l , and a nearby site S_2 having threshold undercooling $T_2 > T_l$. When the temperature reaches $T_{liq} - T_l$, S_1 nucleates and solute is rejected into the surroundings as the solid forms. When the temperature reaches $T_{liq} - T_2$, if the cooling rate is high, the solute concentration at S_2 has not changed because the solute released at S_1 has not had time to diffuse to S_2 , and nucleation can occur. If the cooling rate is low, then solute released at S_1 does have time to diffuse to S_2 , and so the undercooling at that point is not T_2 but is decreased by the amount $m(C-C^o)$ by which the liquidus is depressed. Once enough time has passed, the solid grain nucleated at S_1 will grow beyond S_2 and prevent nucleation at that site. The precise shape of the probability density function for nucleation should have a smaller effect at high cooling rates, reflecting this mechanism of competition between the

nucleation and growth processes and illustrating the desirability of a high cooling rate for producing a refined and reproducible microstructure.

The most significant changes are due to the cooling rate and the nucleation density N_n , whereas the trends for the other parameters are very slight. The choice of nucleation distribution type (quadratic, Gaussian or step) has little effect on the results.

The relationship between the nucleation distribution and the resulting nucleation events is shown in the histograms of Figure 4-19. As the grains grow, some nucleation sites are incorporated into the solid and do not have a chance to form new grains. As grains grow, the solute concentration increases in the liquid thus decreasing the liquidus temperature and hence the driving force for nucleation, preventing the threshold for those nucleation sites from being reached. Therefore the nucleation event histogram drops off at higher undercooling (lower temperature). The model acts as a transfer function between the input nucleation probability distribution and the output nucleation event distribution. Because the microsegregation of dissolved silicon alters the degree of undercooling with respect to the local liquidus, the distribution of nucleation events is transformed again when plotted against the temperature, Figure 4-19 (b).

The result of this transfer is that the distribution of grain nucleation temperature is close to a Gaussian distribution, for each of the chosen input distributions. The sharpness of the low-undercooling side of the step distribution results in a skew in the resulting nucleation distribution, but the quadratic and Gaussian input distributions both have smoothly rising low-undercooling edges (the left-hand side of each graph in Figure 4-19 (a)). However, the high-undercooling edge does not contribute to the final distribution. This represents particles which are less active as nucleating agents than the average. Greer *et al.* [9] have interpreted their experimental observations of the distribution of particles in Ti-B grain refiner and the grain sizes resulting from varying levels of refiner addition to Al castings as showing that only the largest 4% of the observed particle distribution (corresponding to the smallest undercooling) actually nucleate grains. Thus, nucleation distribution models such as the quadratic model of Oldfield [84] and the Gaussian model of Zou [83] could yield identical results for suitable choices of the parameters.

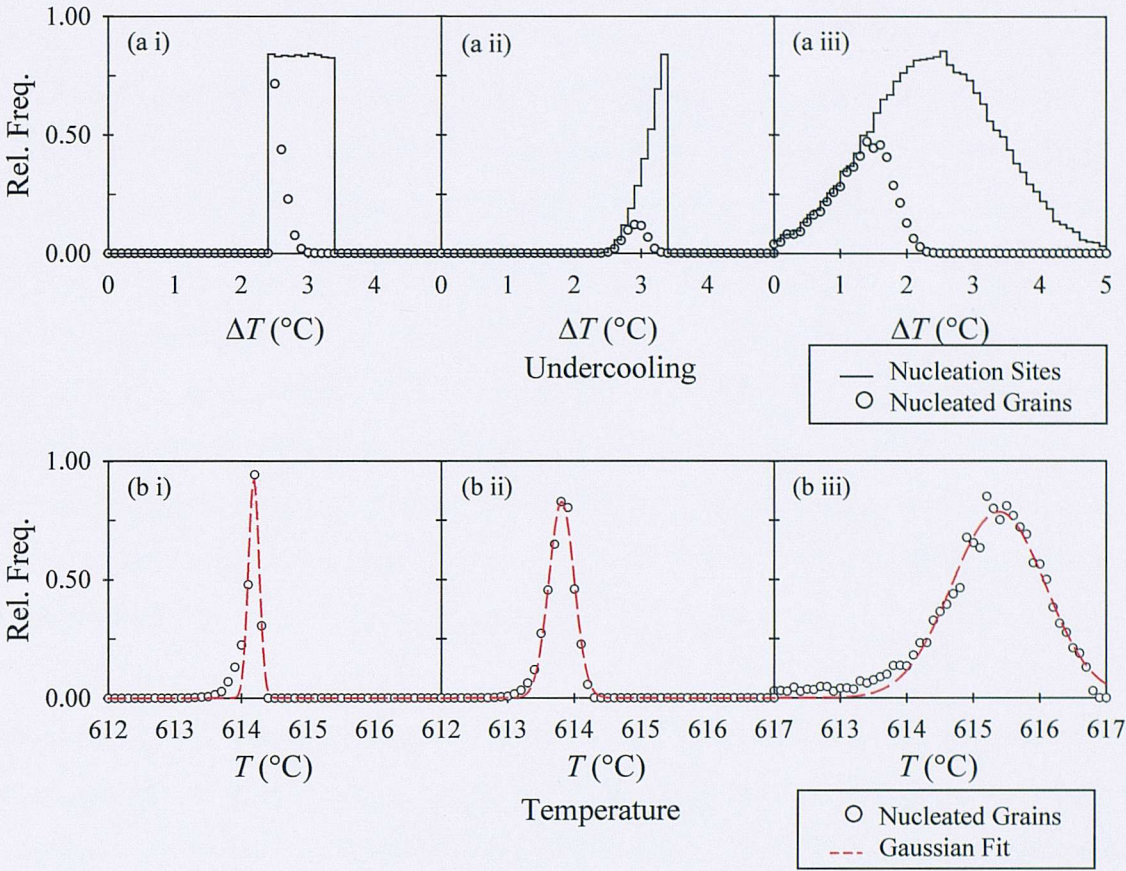


Figure 4-19. Histograms of the distribution of (a) grain nucleation sites and grain nucleation events as functions of undercooling and (b) nucleation events as a function of temperature with Gaussian fitted curves for (i) step distribution, (ii) quadratic distribution and (iii) Gaussian distribution of potential nucleation sites.

4.2. Validation

The validation of the model against analytical solutions for simplified problems demonstrates that the behaviour of the model adequately encapsulates the relevant assumptions.

4.2.1. Response to Cooling Rate—Isothermal-Comparison to Exp.

Increasing the cooling rate during isothermal constant-cooling solidification increases the number of grains, decreasing the grain size, as shown in Figure 4-20 where the model results for Al7Si are compared with the experimental results of Fang and Granger [50], Venkataramani *et al.* [108] and Youssef [109] for A356 in conventional wedge castings at Imperial College. Increasing the cooling rate increases the number of grains and decreases the grain size. If the nucleation parameter N_n is chosen as $1 \times 10^{10} \text{ m}^{-3}$, near to the values reported by Venkataramani for their experiments, the results are in good agreement with their results, and if N_n is increased to $1 \times 10^{12} \text{ m}^{-3}$ the results are in excellent agreement with the results from the grain-refined wedge castings.

The comparison of the grain size from the solidification model with the experiments (Fig. 4-20) shows that the mechanism of competition between the growth and nucleation processes in the model is a good reflection of the physical process. An increased cooling rate favours increased nucleation, since the growth is limited by the diffusion layer of silicon ahead of the interface. The assumption of inert nuclei is able to replicate the trend of this behaviour.

However, the relationship between the grain size and cooling rate differs between the experiments; the results of Greer and of Youssef show much smaller grain sizes than those of Fang and of Venkataramani for similar cooling rates. This is to be expected as different amounts and types of grain refiner were added in the different studies. Therefore a larger value of N_n was required in the model for agreement with the latter experiments. Venkataramani has estimated values of N_n from grain size measurements and these values, on the order of 10^{10} m^{-3} are quite close to the values used in the model.

Directional Solidification

If the model is not isothermal, but instead has a constant temperature gradient applied, which is translated at a constant velocity along the model domain, then the competitive mechanism between the growth and nucleation of grains gives rise to a columnar to equiaxed transition in the grain morphology. This is in turn strongly affected by the number of nucleation sites present. This interaction is shown in Figure 4-22. In Figure 4-22(a) the number density of grains is plotted against the local solidification time and in Figure 4-22(b) against N_n , showing clear relationships, and representative resulting microstructures are shown in Figure 4-22 (b). The shape of the symbol on Figure 4-22 (a) corresponds to the level of N_n used. Within each level, the N_g increases with increasing velocity, and for each velocity N_g increases with increasing N_n as expected; the points in the lower left of the graph correspond to columnar microstructures. Near the transition, the grains are not fully equiaxed but elongated in the growth direction. Light micrographs were made of the samples produced in the directional solidification experiments of Lee *et al.* [110, 111] and are shown in Figure 4-23; the structures compare quite well.

The predictions of Greer *et al.* [9] and their experimental verification also show a linear relationship between $\log(N_g)$ and $\log(N_n)$. The model results are compared with their results in Figure 4-21. To more closely match their assumption, the published results for the particle size distribution were transformed into a nucleation undercooling distribution, according to their formula, and then approximated by a normal distribution such that the low-undercooling

edge had the best match. This was chosen due to the hypothesis that most of the refiner particles with high thresholds for the onset of growth would not be activated. However, the results agree only qualitatively due to the differing nature of the systems being modelled during the growth. (Commercial purity Al with Ti-B grain refiner and excess Ti vs. Al-Si alloy) The results of Maxwell and Hellawall [112] also show a similar behaviour, up to the point at which the growth of the first nucleated grains extinguishes the remaining nucleation sites.

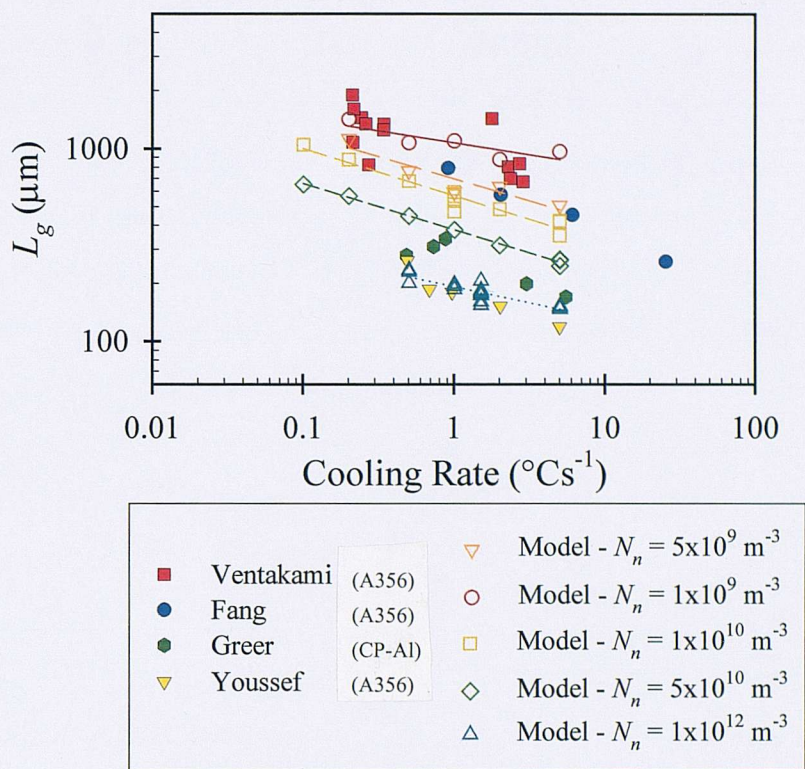


Figure 4-20. Response of grain size to the cooling rate, compared with published results [9, 50, 108] and wedge castings by Youssef at Imperial College [109].

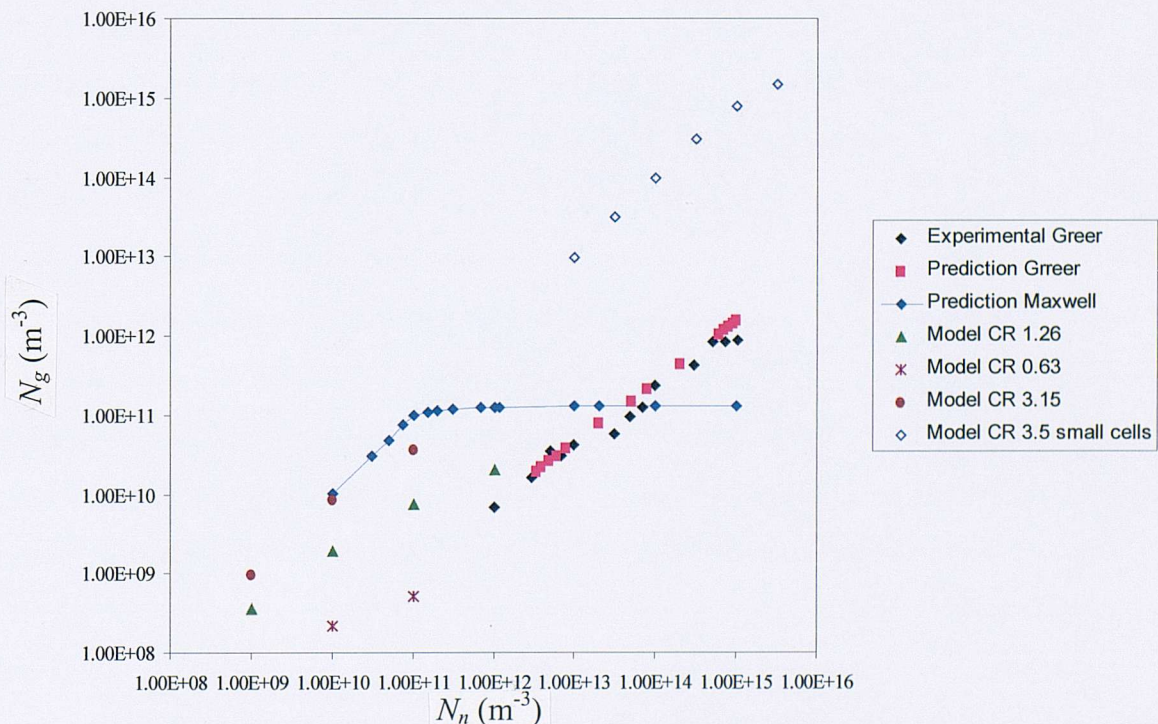


Figure 4-21. Relationship between the number of nucleant particles and the number of nucleated grains, predicted and experimental After Greer *et al.* [9].

The solidification model has been applied to the study of nickel-based superalloys. The grain-growth model has been combined with macroscopic heat and mass transfer models by Xu *et al.* [113] to simulate the genesis of microstructural defects during vacuum-arc remelting of large scale ingots, and by Wang *et al.* [86] to study the formation of misaligned crystals during the directional solidification of superalloy turbine blades. Figure 4-24 compares the primary dendrite spacing predictions of the model with the analytical model of Kurz and Fisher, and experimental results of Davies [114] and Kermanpur [115] with good correspondence. Each of the triangles on the graph represents a stable spacing in the model, showing that the model predicts a range of stability (delimited by dotted lines) for dendrite arm spacing ranging over approximately a factor of two, as predicted by Hunt and Lu [116]. The different stable growth spacings occur in response to different initial configurations of the nuclei.

4.2.2. Pore growth

If a single gas bubble is forced to nucleate in a fully liquid domain in which the dissolved hydrogen is supersaturated, the radius of the resulting bubble follows the growth pattern shown in Figure 4-25 and forms the shape shown in Figure 4-26 (a) which is a grid-like approximation to the expected sphere. This results in an approximately spherical isosurface of the H concentration surrounding the bubble, Figure 4-26 (b). The growth deviates from the expected curve for an infinite domain when the gas in the finite domain becomes depleted. The bubble in the 15.6 mm³ domain deviates from the expected $r=t^{0.5}$ curve at a smaller radius than that in the 125 mm³ domain. The initial point is offset from the origin because of the finite starting size of the initial nucleus.

The preceding sections show that the solidification and diffusion model, though not perfect, provides an acceptable framework of grain structure which can respond to the applied casting conditions. Putting together this model with the pore growth model and using a similar nucleation model for the pores will form the basis for the following chapters, in which the model is applied to specific problems in the solidification of aluminium alloys.

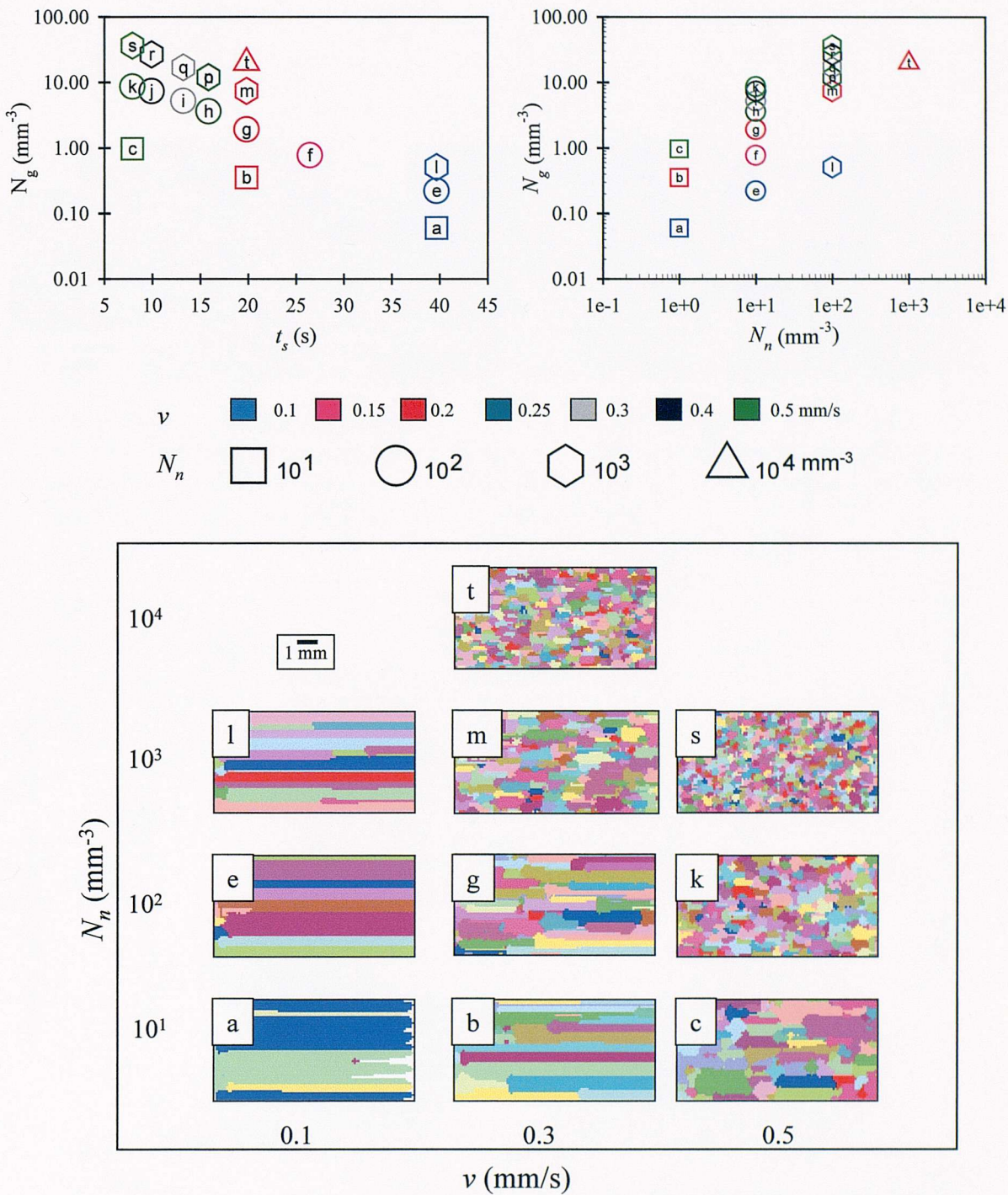


Figure 4-22. The effect of directional solidification and grain nucleation on the microstructure. (a) Grain number density response to changing velocity for several levels of nucleation site density plotted against local solidification time t_s . (b) The same results plotted against the site density N_n . (c) Simulated microstructures for selected examples, showing the regimes of columnar, transitional, and equiaxed grain structure.

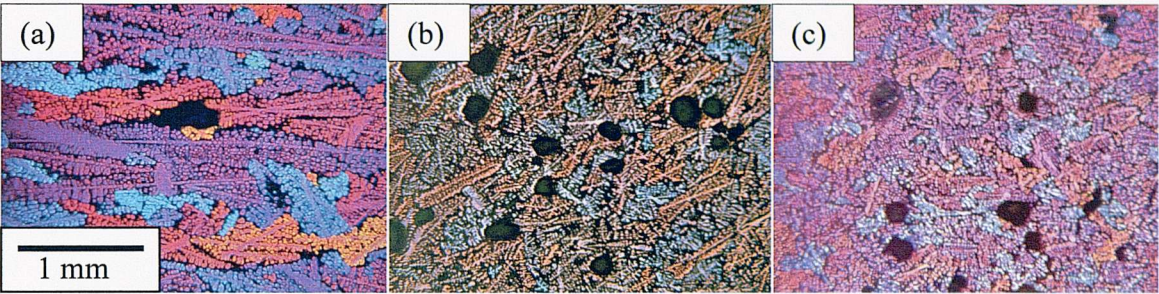


Figure 4-23. Light micrographs of directionally solidified Al7Si alloy as described by Lee [110] showing columnar to equiaxed transition as the velocity is increased; (a) $v=0.10$ mm/s, (b) $v=0.25$ mm/s, and (c) $v=0.48$ mm/s. (Anodised using Barker’s etchant and imaged with polarized light.)

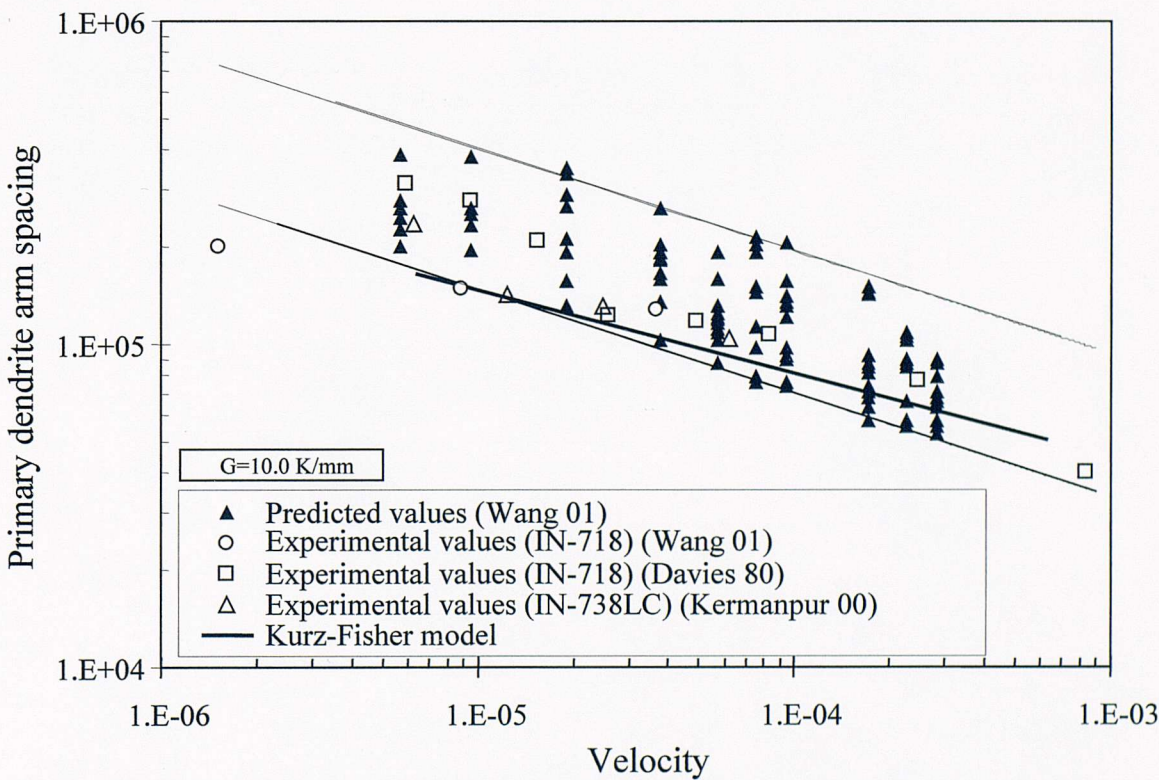


Figure 4-24. Predictions of the model for the dendrite arm spacing in directionally solidified IN718 nickel-based superalloy, compared with experimental results and analytical models. After Wang *et al.* [86].

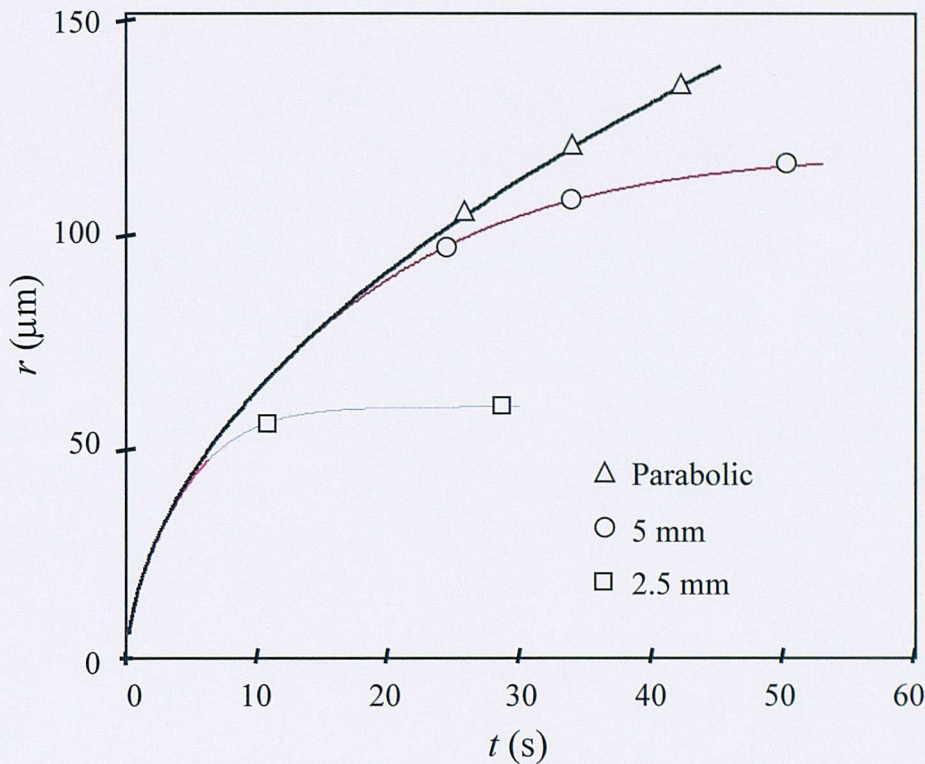


Figure 4-25 Growth of a single bubble in fully liquid, constant temperature domains, a 2.5 mm cube of 25x25x25 cells, and a 5mm cube of 50x50x50 cells. The initial supersaturation of H was three times the equilibrium value. The radius as a function of time is compared with the expected square-root curve.

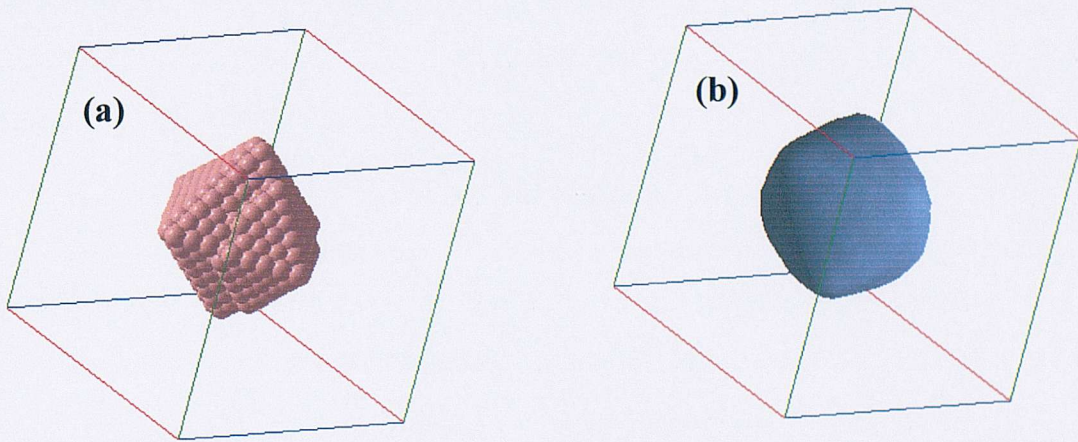


Figure 4-26 The shape adopted by the growing bubble upon the discrete grid. (a) Each cell in the bubble is represented by a small sphere. (b) The isosurface of H concentration surrounding the bubble.

5. THE POROSITY MODEL

This chapter focuses on the modelling of the behaviour of gas pores in the solidifying alloy. The processes of pore nucleation and growth, the stochastic effects of the random configuration of nuclei, and the effects of varying some of the physical and chemical properties upon the model results are studied. The effects of interactions of the solidification and porosity model parameters are explored by studying a two-level factorial experimental design applied to the model, to determine the relative magnitude and significance of the interaction effects. Finally, the results of applying the single bubble surface model to a simplified geometry are presented, showing qualitative agreement with, and hence the usefulness of, the assumptions used to build the restricted growth model for the pores.

5.1. Responses

The specific measures of the porosity used in this chapter and in the following application chapters are:

- The equivalent spherical pore radius, R , which is calculated from the volume of the gas in each pore, under the assumption of spherical shape. The average R of all the pores, R_a , and the maximum in the domain, R_m , are used as measures of the overall pore population. Unless otherwise indicated, these population responses are calculated for a particular temperature; in a directional solidification simulation this is not necessarily equivalent to the average at a particular time.
- The maximum pore length L , which is calculated from the minimum and maximum grid cells occupied by the pore in each of the three coordinate directions. In other words, L is the body diagonal of the minimal coordinate-aligned rectangular solid entirely containing the pore calculated from the coordinates of the extreme cells,

$$L = \sqrt{(x_{\min} - x_{\max})^2 + (y_{\min} - y_{\max})^2 + (z_{\min} - z_{\max})^2} \quad (5-1)$$

where x , y , and z are the co-ordinate directions and the subscripts *min* and *max* indicate the minimum and maximum values among the cells in the pore. Pores that wrapped through the periodic boundary of the domain were neglected to simplify the calculations. For each pore occupying only a single cell, the equivalent spherical diameter is used. The maximum in the whole population is designated L_m . This measure is not applicable to the spherical pore model as only a single cell is associated with each pore. This is illustrated for a two-dimensional case in Figure 5-1.

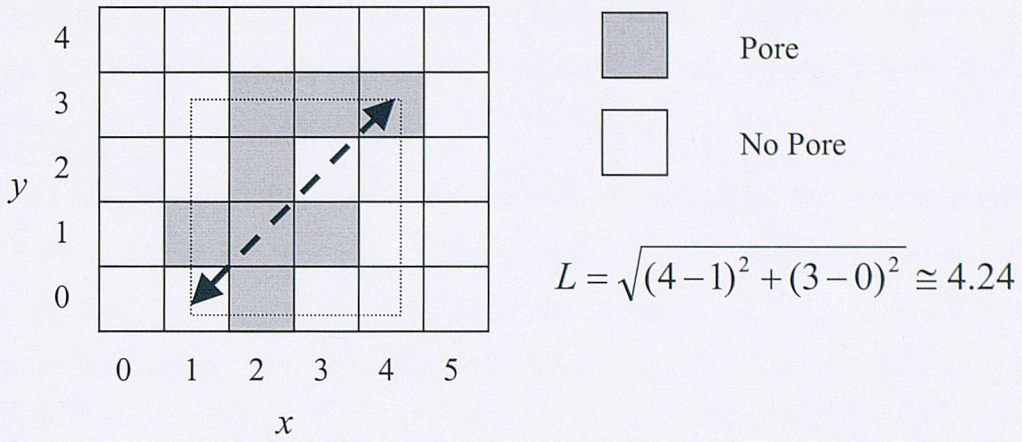


Figure 5-1. The pore length L in the multi-cell pore model approximated as the diagonal of the bounding box.

- The pore number density per unit volume, N_p .
- The percentage porosity, P , calculated as the ratio of the total pore volume to the total domain volume.

Furthermore, the solidification model only has a very rudimentary mechanism for calculating the eutectic behaviour which tended to create a large amount of spurious pore nucleation just at the eutectic point, so the final state was chosen as the state at one degree C above the eutectic point.

5.2. Single Experiments

To clarify the results produced by the model and used in the following application chapters, some individual modelling experiments are analysed in detail.

5.2.1. Pore Nucleation

The model for the nucleation of pores behaves in a similar fashion to that for the nucleation of grains. Some differences arise because the diffusivity of hydrogen is greater than that of silicon or magnesium in the liquid and especially in the solid. This results in a greater length scale for the interaction of nucleation sites with sources (growing solid phase) and sinks (growing pores) of hydrogen compared with the length scale over which growing solid interacts with grain nuclei. Furthermore, the action of growing pores sinking hydrogen has no analogue in the grain nucleation model.

The nucleation of a specific pore occurs if a cell containing a nucleation site reaches a predetermined supersaturation ratio S_{th} which is different for each site, as described in Section 3.2.1. The degree of supersaturation depends upon the amount of hydrogen dissolved in the cell, the temperature, the fraction of solid in the cell, and the amount of dissolved alloy

components, as described by Equation 3-21. The amount of hydrogen depends upon the interaction of the source due to partitioning of H at the advancing solid-liquid interface, and the sink due to the growth of pores.

The interaction of these processes causes some sites to nucleate pores whereas others do not. As previously described for the grain nucleation, Section 4.1.7, those sites having a greater s_n have less likelihood of nucleating a pore. The temperature at which this occurs depends upon the degree of local enrichment of hydrogen. This results in distributions of nucleation events similar to the example shown in Figure 5-2(a). The subset of predetermined pore nucleation sites having s_n nearest to s_{th} are most likely to nucleate pores; as s_n increases the proportion of sites actually nucleating pores decreases. For the step distribution of sites this results in the exponentially decreasing distribution in Figure 5-2(a). The temperature of the resulting nucleation events, Figure 5-2(b), shows a peaked distribution which approximates a Gaussian distribution truncated at high temperature and with a tail towards the low temperature.

5.2.2. Pore Growth

The growth of pores in the model differs from the growth for a single pore shown in Section 4.2.2 due to the changing environment. The H concentration, solubility, and diffusivity are changing, and in the complex pore model the ability of the pore to expand is decreased as the fraction solid increases and the limiting radius decreases.

The growth of pores in the spherical model is shown in Figure 5-3. The growth of each pore is characterized by a sharp initial increase in radius, followed by a gradual decrease in growth rate. The decrease is more than that predicted for a single pore in an infinite liquid, indicating that those effects that decrease the availability and transport of hydrogen exceed the effect of the increase in dissolved hydrogen due to partitioning. The radius R of each pore may be approximated as:

$$R = At_g^\alpha, \quad (5-2)$$

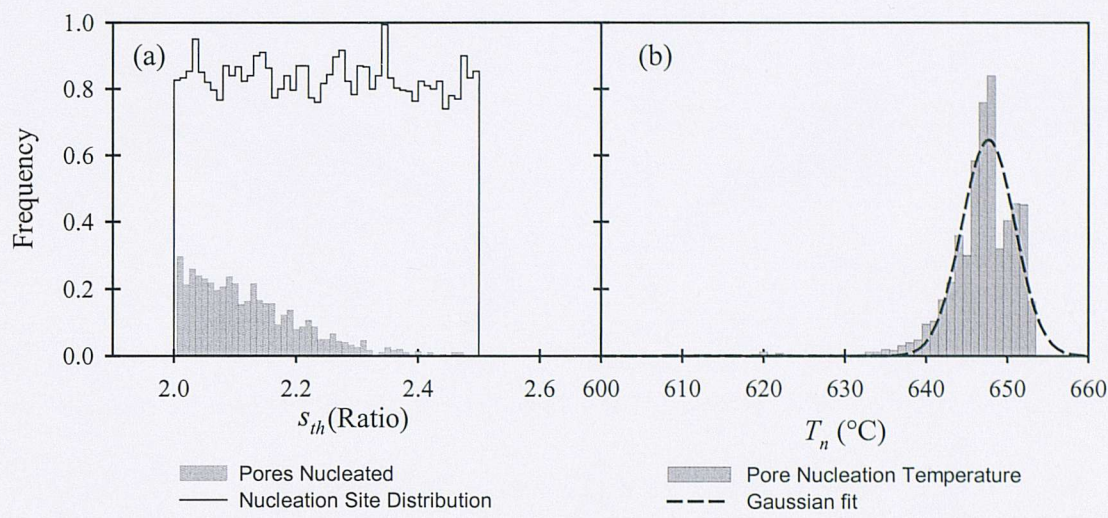


Figure 5-2. The resulting distribution of simulated pore nucleation events. (a) The hydrogen supersaturation ratio at nucleation, s_{th} , for all pores compared with the input distribution of potential nucleation sites. (b) The nucleation temperature distribution for all pores with a fitted Gaussian curve.

where α would be 0.5 for an isolated pore, as in Equation 2-33 and t_g is the time measured from the nucleation of that pore. The results of fitting equations of this type to each pore are shown in Figure 5-4, and the values of α are mostly between 0.35 and 0.45 with a mean of 0.4. The values of the parameter A also vary, from 25 to 50 μm with a mean of 38 μm . The A value primarily depends upon the initial effective diffusivity and supersaturation condition for the pore, and the effective α value upon the change in these properties as time progresses. It is possible that such results could be used to develop a statistically based model which would produce similar results for the pore population responses, at much less computational cost, thus allowing the application to larger castings. This would be an intermediate level of detail for the simulation, between the level used for this model and that using the regression equations, described in the next chapter.

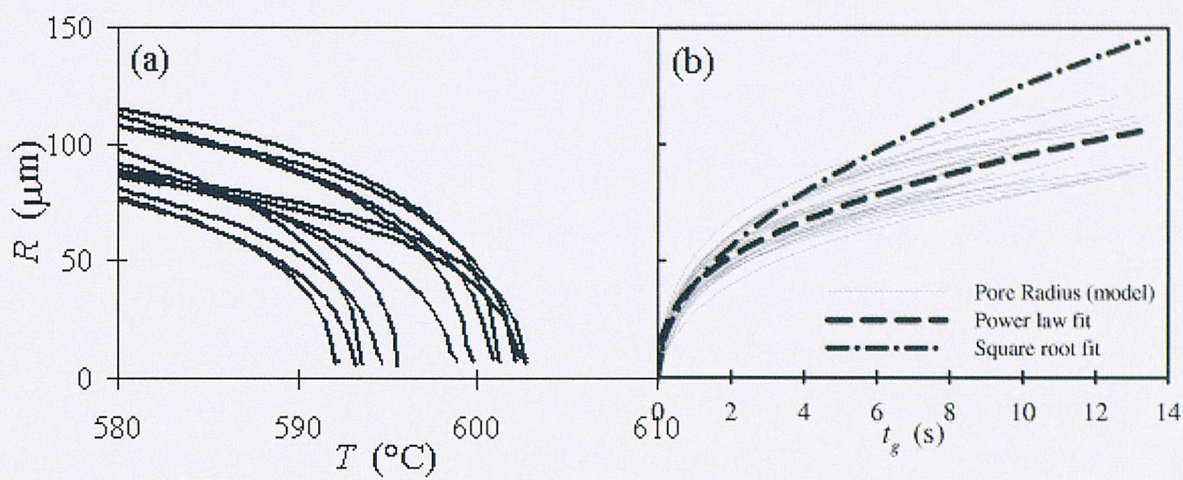


Figure 5-3. Individual pore radius results. (a) As a function of temperature. (b) As a function of time for growth t_g , with power-law and square-root law approximations.

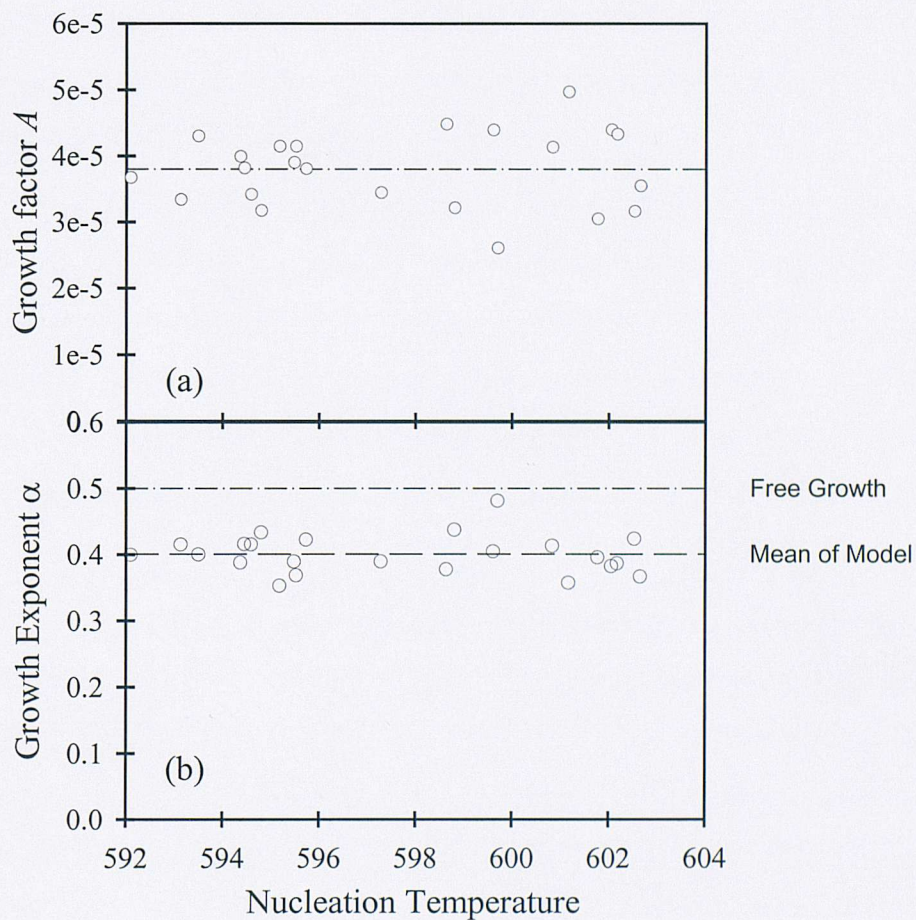


Figure 5-4. The results of fitting a function of the form $R = At_g^\alpha$ to each of the pore growth curves in Figure 5-3.

5.2.3. *Distribution of Pore Size*

The pores in the model have a range of final sizes. The distribution of equivalent spherical radius for the whole population of pores for four different simulations, using the parameters given in Table V, are shown in Figure 5-5. Graphs of the relationships between the pore size and the nucleation temperature are shown in Figure 5-6. Increasing C_H^i increases the radius and also spreads out the distribution (*e.g.* changing from 5-5(a) to (b), or from (c) to (d)) due to earlier nucleation, more rapid growth, and more time for growth before solidification. The scatter in size among those pores which nucleate at higher temperature is greater than the scatter among those which nucleate at lower temperature as seen from the spread of the data points at the high temperature end of Figure 5-6(b) and (d). Decreasing the velocity, v , also spreads out the size distribution, and decreases the overall number (*e.g.* changing from 5-5(a) to (c), or from (b) to (d)) resulting in the very flat distribution seen in figure 5-5(d) if C_H^i is increased and v is decreased. This is usually not a desirable distribution of porosity; not only are there especially large pores but the distribution does not allow reliable prediction of the expected pore size from a random sample.

The complex pore model predicts the formation of some significant large pores. The histograms in Figure 5-7 are for cases using 100x50x50 cell domains with 100 μm cells; the parameters are given in Table VI. Case (a) shows a few pores up to 5 mm in length, whereas those in case (b) do not exceed 300 μm . The histograms only include the pores that extend over more than one cell. In case (a) there were 50 single-cell pores, whereas in case (b) there were 20,000 single-cell pores. A full two-level four-factor set of simulations is analysed in Section 5.6.

The equivalent radius does not convey the same information; Figure 5-8 shows histograms of the equivalent radius of the pores from the same simulations. The maximum in case (a) is only 250 μm (diameter of 500 μm). The conditions for case (a) favour the formation of interconnected 'wormhole' porosity and would likely produce poor quality castings. The occurrence of the long pore could not easily be predicted from the equivalent spherical radius results, Figure 5-8, or the results of a spherical pore model. However, the pore of maximum length is the most significant for the mechanical properties of the final object, especially the resistance to fatigue. In alloys where the fraction of solid is high when the pores are growing, and where the fraction of eutectic is small, the limited radius and hence the extended shape of the pore is more likely to occur, and the complex pore model is a better approximation.

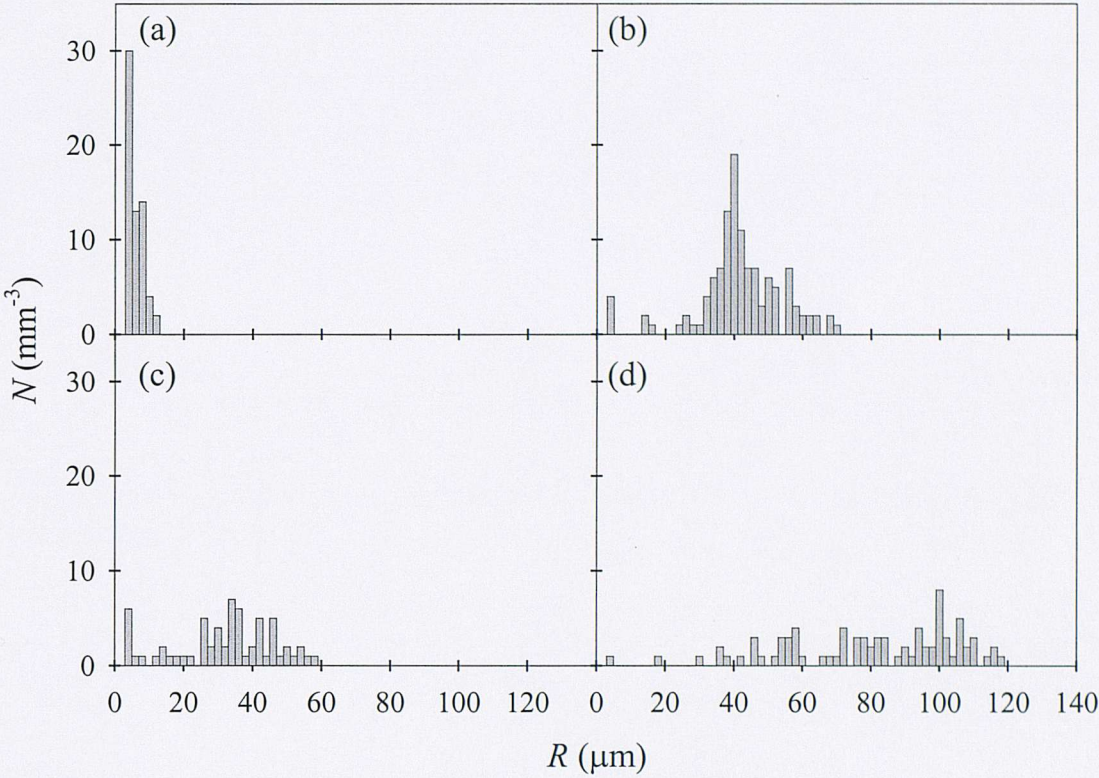


Figure 5-5. Histograms of the size (equivalent spherical radius) for a population of simulated pores in each of four experiments, (a), (b), (c), and (d), using the parameters given in Table V.

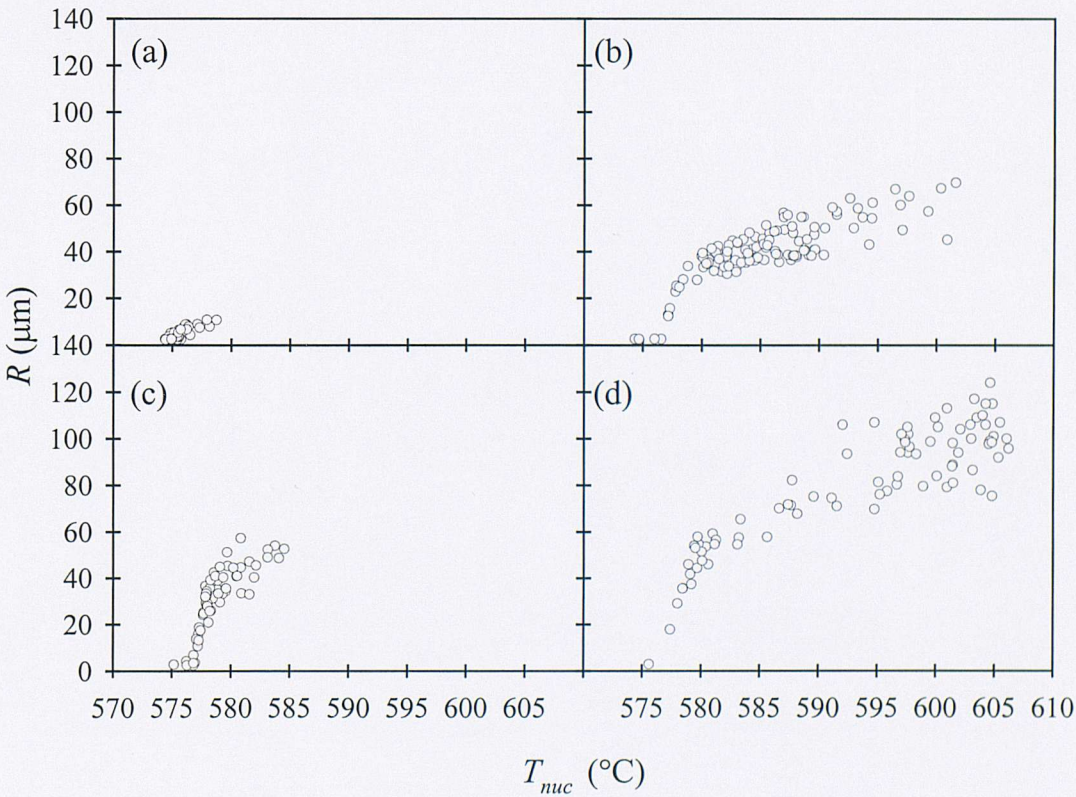


Figure 5-6. The relationship between final pore size and pore nucleation temperature, for each of the experiments (a), (b), (c), and (d), using the parameters given in Table V.

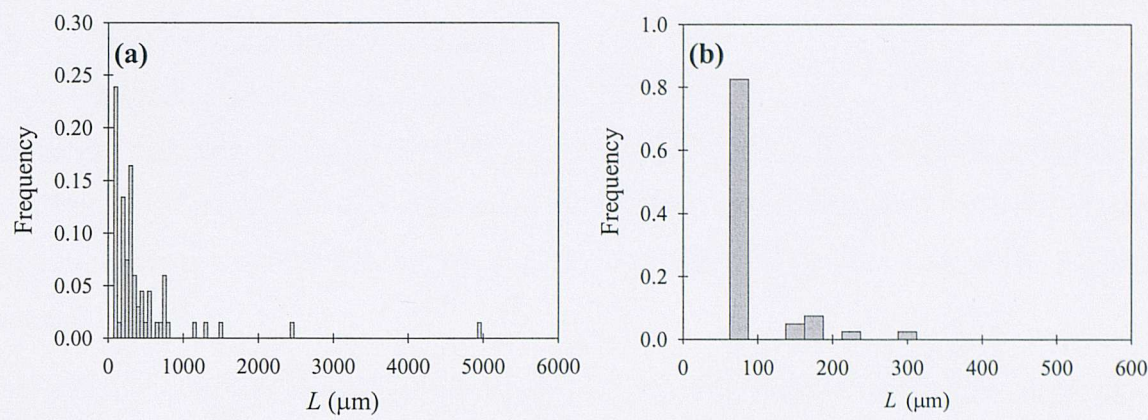


Figure 5-7. Histograms of the pore length L in two simulations using the parameters in Table VI.

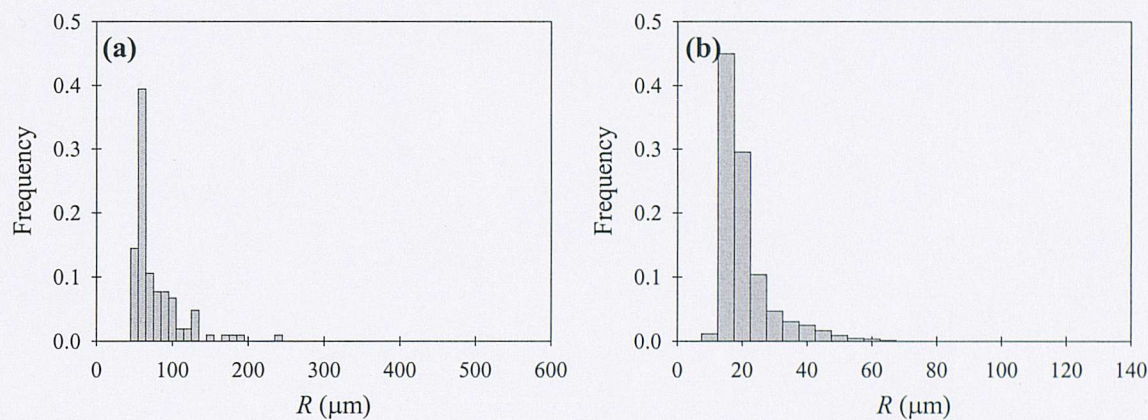


Figure 5-8. Histograms of the pore radius R in two simulations using the parameters in Table VI.

Table V. Parameters Varied for Figure 5-5.

	ν (mm s ⁻¹)	C_H^i (ml/100g STP)
(a)	2.00	0.21
(b)	2.00	0.47
(c)	0.50	0.21
(d)	0.50	0.47

Table VI. Parameters Varied for Figure 5-7.

	ν (mm s ⁻¹)	C_H^i (ml/100g STP)	N_p (mm ⁻³)
(a)	0.20	0.17	50
(b)	0.50	0.43	500

5.3. Variation Between Experiments

5.3.1. *Distribution of Averaged Responses*

The actual maximum size also depends upon the initial arrangement of grain and pore nuclei for a particular set of casting conditions. A set of fifty simulations with identical conditions was run in which only the random seed value, hence the initial positioning of the nuclei, was changed.

The effect of the initial spatial distribution of the potential nuclei on the final porosity responses was examined by running several trials in which the random number generator seed value was changed whilst keeping all other inputs constant. This indicates the degree by which the responses change due to differences in the arrangement of nucleation sites and their potential. The results are shown graphically in Figure 5-9 and the statistical summary of the 50 runs is given in Table VII(a).

Table VII.

(a) Summary statistics from 50 spherical model simulations.

	R_a (μm)	R_m (μm)	P (%)	N_p (mm^{-3})
Mean	68.89	101.21	0.04	0.33
Median	68.20	101.89	0.04	0.31
Standard Deviation	6.37	8.16	0.01	0.07
Skewness	0.30	-0.06	1.11	0.06
Range	32.76	32.24	0.06	0.31
Minimum	51.98	85.45	0.02	0.16
Maximum	84.74	117.70	0.09	0.47
R^{2*}	0.04	0.02	0.02	0.008

(b) Summary statistics from 50 multicell pore simulations.

	R_a (μm)	R_m (μm)	P (%)	N_p (mm^{-3})	L_m (μm)
Mean	39.11	150.43	0.69	3.08	521.82
Median	38.98	150.63	0.69	3.09	505.03
Standard Deviation	0.86	7.16	0.03	0.22	62.25
Skewness	0.28	0.17	-0.04	-0.01	0.85
Range	4.54	41.35	0.12	0.90	294.40
Minimum	37.03	130.65	0.63	2.66	409.89
Maximum	41.57	172.00	0.75	3.56	704.29
R^{2*}	0.11	0.001	0.002	0.01	0.02

**The coefficient of correlation with respect to the random seed value.*

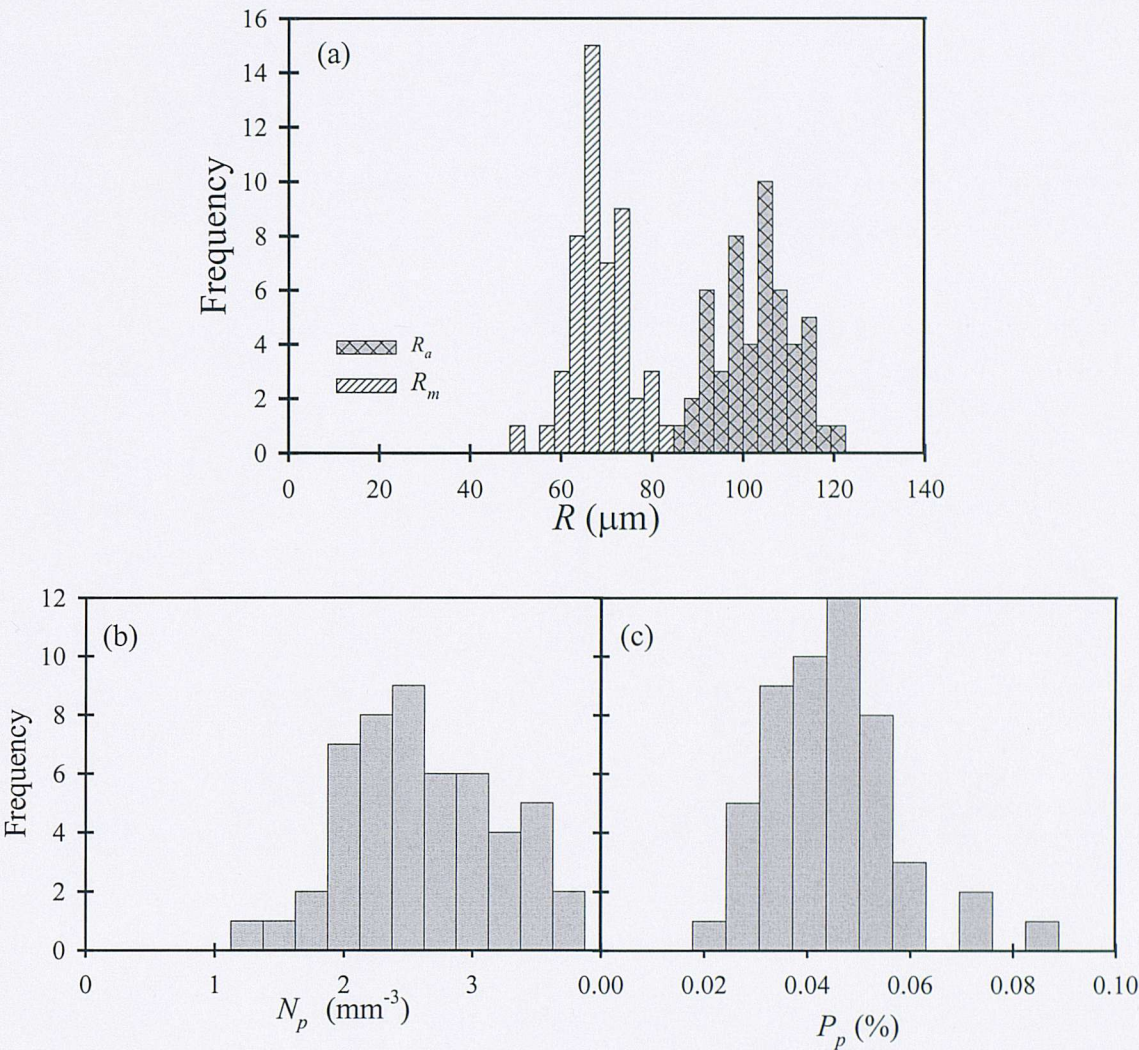


Figure 5-9. Histograms of (a) average (R_a) and maximum (R_m) equivalent spherical pore radius, (b) pore number density and (c) percentage porosity from a spherical pore model repeated 50 times with random variation in the starting configuration.

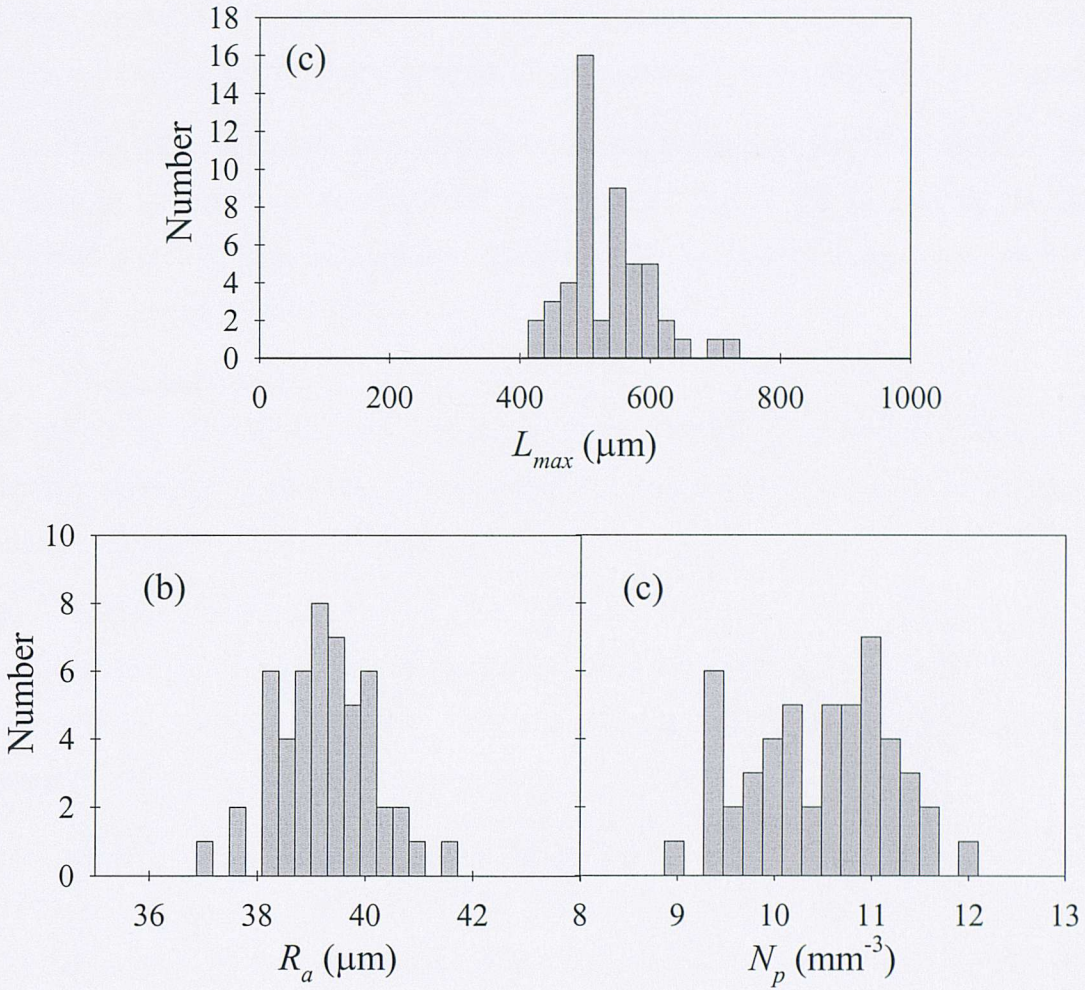


Figure 5-10. Histograms of (a) the maximum pore length L_{max} , (b) the average equivalent spherical radius R_a , and (c) the number density N_p of pores in each simulation for 50 simulations differing in the random number used to generate the initial configuration.

This variation causes a significant scatter in all the responses, and the scatter in the number density of pores is the greatest. The final number density depends greatly on the proximity of nuclei having low thresholds to other nuclei. The scatter in the maximum pore radius is greater than that of the average pore radius, since the former also depends upon the fortuitous arrangement of nuclei -- if a low-threshold nucleus occurs in an area that remains liquid to low temperatures, it will have a large radius.

The results of these simulations indicate the degree of scatter which may be expected between model runs in any simulation experiment. The other model results therefore exhibit various trends superimposed upon this baseline scatter. The scatter does not depend in any measurable way upon the seed number variable, as indicated by the low coefficient of correlation R^2 . This behaviour mimics what might be observed if one were to experimentally examine small

samples approximately the size of the model domain in which the average distribution of nuclei was similar, but the exact location of the nuclei within the sample was uncontrolled.

In the multicell pore model, the effect upon the maximum pore length is relatively greater, as the change in length of an elongated narrow pore due to the change in amount of gas contained is greater than for a sphere. The results for 50 separate simulations are summarized in Figure 5-10 and Table VII(b).

5.4. Sensitivity Study

The effects of varying the initial hydrogen concentration, hydrogen equilibrium solubility, effective diffusion coefficient, and system pressure were determined in the model. The combined results are shown Figure 5-11.

5.4.1. Material Properties

Increasing the initial hydrogen concentration increased the final pore radius and percentage porosity (Figs. 5-11(a) and 5-11(c)). At the lowest value of initial hydrogen content, no pores were nucleated because supersaturation did not occur above the eutectic temperature.

The equation for hydrogen solubility in the mushy zone was extrapolated from very limited data for temperatures significantly above or below those simulated. There was some concern over the validity of this extrapolation; therefore the effect of varying this thermophysical property was studied. Increasing the solubility decreases the final pore radius and percentage porosity in the model, whilst increasing the pore number density. This is the inverse effect of hydrogen concentration, as expected.

Increasing the effective diffusion coefficient, D_e , increased the average pore size and decreased the total number of pores. By increasing the diffusion rate, more hydrogen reached the pores faster, enhancing their growth. An increased diffusivity with respect to the baseline case allowed the sink action of those pores nucleating early to lower the hydrogen concentration to a greater extent and at a greater distance, thus preventing the concentration in cells containing nucleation sites from reaching their threshold. The pores that do nucleate then have access to larger amounts of hydrogen, which is incorporated faster. The combination of these effects causes the overall percentage porosity to increase despite the decrease in pore density. As might be expected, decreasing D_e had the reverse effect.

5.4.2. System Pressure

It was assumed that the pressure drop in the experiments was negligible; however, this is usually not the case in an industrial casting. Therefore, the model's response to the

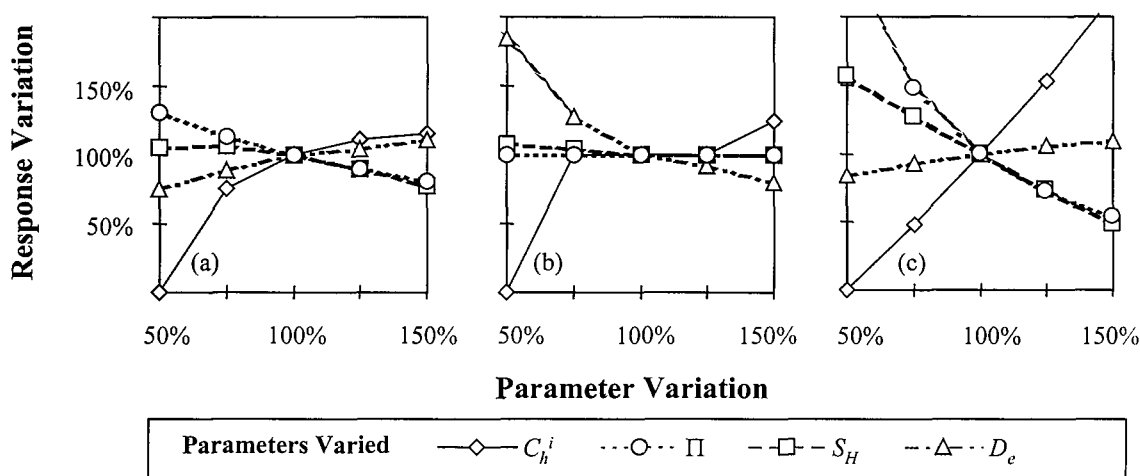


Figure 5-11. The relative effect on the responses (a) R_a , (b) N_p , and (c) P due to changes in initial hydrogen concentration, pressure, solubility of hydrogen, and diffusivity for the Gulliver-Scheil model.

incorporation of shrinkage (and applied pressure) was determined by testing the sensitivity to the applied pressure. The model demonstrated the expected trend; decreasing pressure increases the average final pore radius and percentage porosity.

5.4.3. Nucleation Distribution

Both the sensitivity study results above, and the comparison to experimental results below, were performed with a rectangular step distribution described in the theory section, with activation thresholds distributed from 1.7 to 2.2 times the equilibrium saturation. To test the sensitivity to the nucleation distribution, three different rectangular step distributions were tested: R1 - baseline case, R2 - shifted to a higher supersaturation, and R3 - a narrower, but higher, step height, using the parameters in Table VIII. All initial conditions except for the nucleation function were the same as the other sensitivity studies.

The predicted histogram of nucleation events as a function of temperature is plotted in Fig. 5-12 for the three cases, together with the plot of fraction solid vs. temperature. Although the input distribution is rectangular, the model acts as a transfer function with the number of activated nuclei being very different from the input distribution of potential nuclei. The number of pores formed in each case is equal to the area under the curve in Fig. 5-12. Using a higher step increases the number of pores (N_n increases by 22% for case 3 over the baseline case 1). Interestingly, the average pore radius only differs by a few percent between these two cases - the increased numbers of pores more effectively sink the available hydrogen, producing a larger number, but only slightly smaller pores.

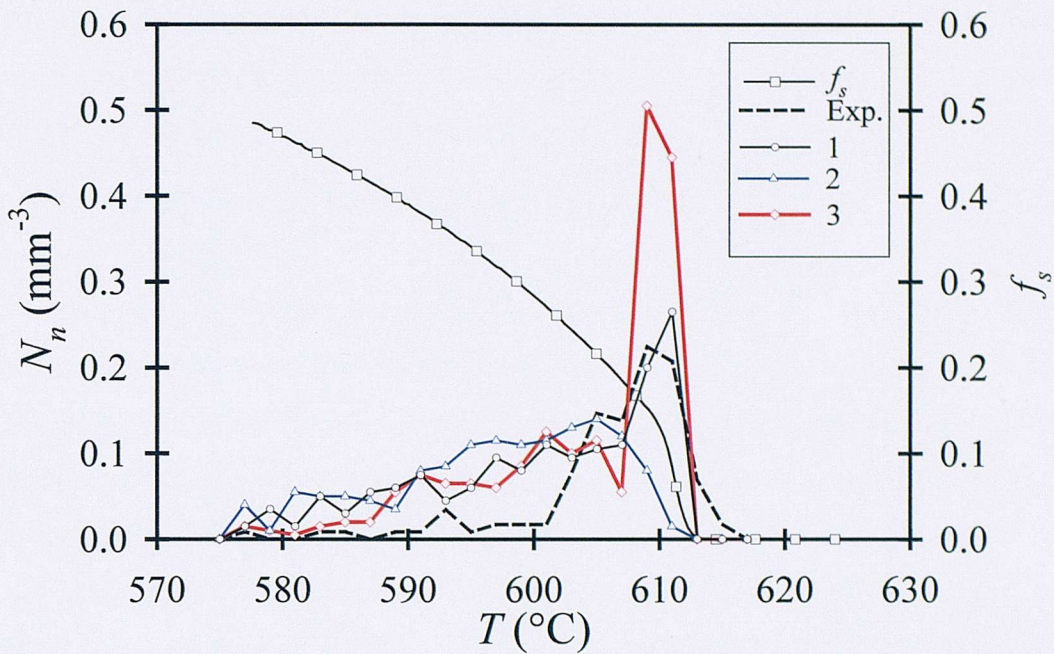


Figure 5-12. The number of nucleation events as a function of temperature in the CA model for three different nucleation input distributions: 1 - baseline case, 2 - shifted to a higher supersaturation, and 3 – a narrower, but higher, step height. The fraction solid versus temperature curve is superimposed for comparison (right axis).

Table VIII. Parameters for experiments in Figure 5-12

case	s_{min}	s_{max}	N_n
	Ratio	Ratio	mm^{-3}
1	1.27	3.27	4.0
2	1.5	2.5	4.0
3	1.27	2.27	4.0

When the minimum threshold is increased to 1.50 (case 2), the spike in the nucleation-temperature histogram just below the liquidus temperature disappears. In the baseline case, the buildup of hydrogen (due to the advancement and impingement of the modelled dendrite tip areas) results in local hydrogen concentrations which exceed the lower threshold and the sharp, stepped input nucleation distribution results in a large ‘wave’ of nucleation near to T_L . Increasing the minimum threshold eliminates the high nucleation levels at the higher temperatures; however, the amount of nucleation at lower temperatures is increased since the sinking of hydrogen is less effective. The final average pore radius for case 2 is only a few percent smaller than the baseline case, although the number of pores has decreased, and hence the percentage porosity predicted is reduced by 14%.

The predicted final pore radius and percentage porosity was found to be most sensitive to the initial hydrogen content and the local pressure, two casting parameters that are considered experimentally to be amongst the most important.

5.5. Effect of Directional Solidification

5.5.1. Gas Diffusion

The behaviour of the gas concentration differs from the solute concentration in two major respects: the diffusivity is greater, and the pores act as sinks, absorbing hydrogen. This results in the behaviour shown by the profile curves of the hydrogen concentration in Figure 5-13. The diffusion of hydrogen away from the advancing solid interface produces a profile of concentration which is initially similar in form to that of the alloy solute, but much larger in extent, resulting in the C_H profile in curve (a). Eventually, the high point may reach the degree of supersaturation required to initiate nucleation, as in curve (b), and some pores form. The concentration of hydrogen in the pore cells is lowered to the equilibrium value accounting for the curvature of the pore surface, and the profile resembles curve (c), where a 'wave' of hydrogen moves along the model domain and the supersaturation falls behind this zone.

When this wave reaches the end of the domain, the supersaturation everywhere relaxes to a uniform profile, varying from place to place depending upon the size and approximated shape of the pores, and the profile is given by curve (d). When the solid around a pore increases sufficiently, the pressure required to expand the pore is greater than the pressure produced by assuming that the hydrogen enters the pore with the volume remaining constant, as described in Equation 3-28 and the pressure in the pore and the supersaturation of the surrounding material increases, as in curve (e). As the temperature falls, the pressure and the solubility both decrease but hydrogen enters the growing pores fast enough to reduce the dissolved hydrogen to the equilibrium amount, curve (f).

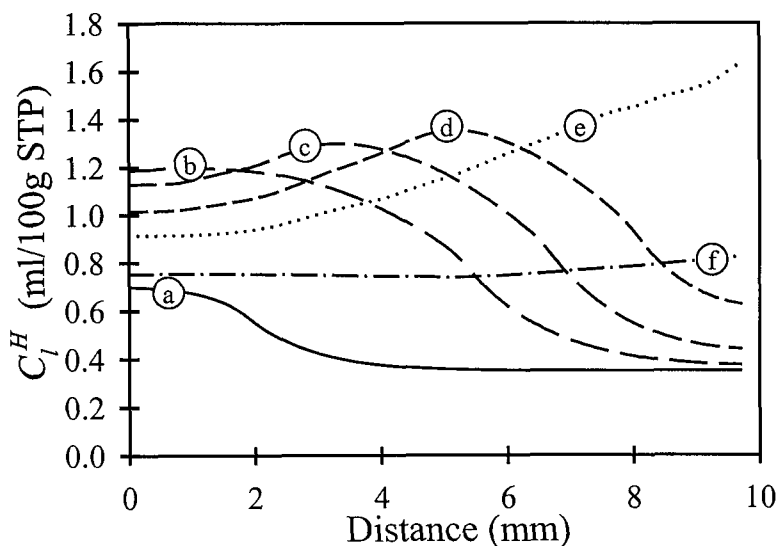


Figure 5-13. The hydrogen concentration profile during directional solidification, averaged over each isothermal slice. Profiles at six different times are shown, lettered in chronological order. (a) 15 s (b) 33 s (c) 39 s (d) 46 s (e) 55 s (f) 90 s.

The effects and magnitudes of these different regimes depend upon the balance between the rate of H buildup due to solidification, the rate of H sinking due to pore growth (which may be restricted by the solid), and the nucleation of pores. This is shown by the series of renderings of the model results in Figures 5-14 through 5-16. In each case, the domain has symmetric boundary conditions at the right hand side, periodic at the top, bottom, front and back, and no diffusion at the left hand side. The right hand side then corresponds to the centre of a plate casting. Each of the simulations had an imposed temperature gradient of 6300 K mm^{-1} .

5.5.2. Low velocity

At very slow velocities, the diffusion of hydrogen is fast enough to result in equal concentration everywhere in the liquid, and the diffusion of silicon is fast enough to allow a coarse columnar grain structure. The formation of hydrogen pores occurs late in the solidification process, when the C_H^l has increased everywhere to the value providing minimum threshold supersaturation s_{min} in the coldest liquid. The grain structure is coarse, and much of the hydrogen is pushed to the hot end of the domain. The pores nucleate either in the liquid channels separating the dendrites, or in the final liquid to solidify. This situation is analogous to centreline porosity forming in a casting under these conditions. A small number of pores form, but the pores can become large. The slow change of the temperature and of the

amount of solid, allows the gas in excess of the saturation limit to be absorbed by the pores, therefore the degree of supersaturation decreases everywhere in the liquid once pores have formed. Pore growth dominates over pore nucleation in this case. Figure 5-14 shows some elongated worm-hole porosity and large pores at the hot (right-hand) end of the domain, for a directional solidification simulated at 10^{-4} m/s.

5.5.3. *Intermediate velocity*

With increasing velocity, the grain structure becomes finer though still columnar. The liquid can persist to lower temperature as there is a greater degree of constitutional undercooling. Due to the decrease in hydrogen solubility with decreased temperature and increased silicon concentration, the supersaturation s_H is greater in this liquid even though the hydrogen concentration is equilibrated in the liquid, and this is where nucleation of the pores is more likely.

These conditions can lead to more wormhole type porosity, in which the pores grow between the columnar grains, if there is sufficient hydrogen to feed such growth. This in turn is determined by the spacing and size of the pores, so that if there are a larger number of pores it is more likely that the pore growth will be cut off by the solid growth. Likewise, if there are a large number of grain nucleation sites, the grain structure is more equiaxed and the pores are more likely to be cut off. This results in a greater number of smaller pores, as the results of a directional solidification simulation at 2×10^{-4} m/s in Figure 5-15 show. There are some elongated pores, but they are much shorter than those seen in Figure 5-14, and there is a scattering of pores smaller than the model cell size (represented by single black spheres.)

5.5.4. *High velocity*

At high velocity the diffusivity of hydrogen plays a greater role. The concentration of hydrogen is not equilibrated in the liquid and so the variation in the hydrogen content is localized near sources (growing solid) and sinks (pores). This allows the supersaturation near the growing solid to remain in the range required for nucleation despite the sinking of hydrogen into the pores. Therefore, nucleation occurs more continuously as growth proceeds, resulting in distributed and small porosity. The results of a directional solidification simulation at 5×10^{-4} m/s in Figure 5-16 show that the pores which have formed in this simulation do not extend over more than one model cell each and do not connect to one another.

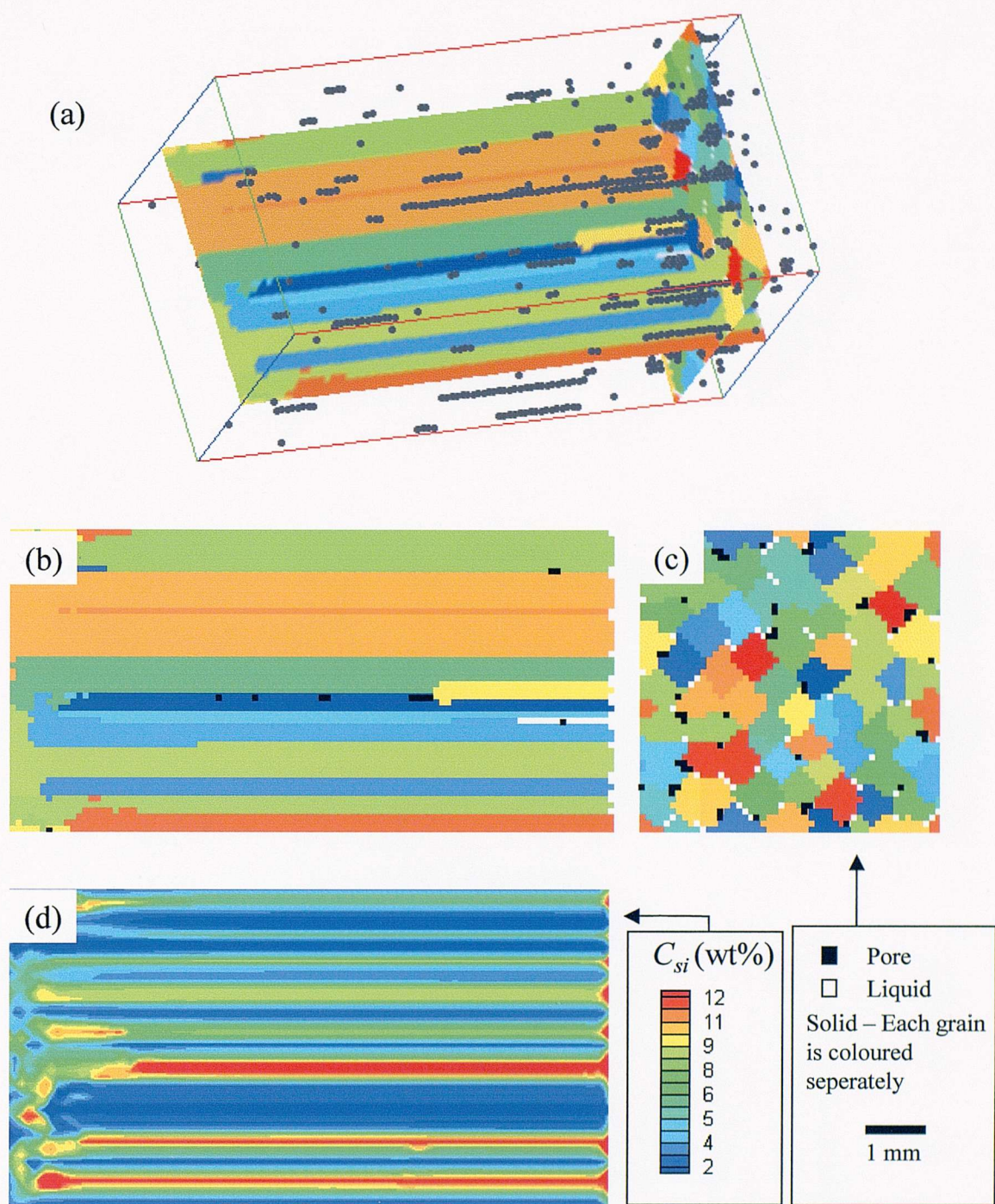


Figure 5-14. Directional solidification at $v=1 \times 10^{-4}$ m/s. (a) Three-dimensional image of the pores in the domain, with section planes indicated. (b) Image of the longitudinal section and (c) cross section, showing the grain structure and pores. (d) Longitudinal section showing the final segregation of silicon (the pores are omitted).

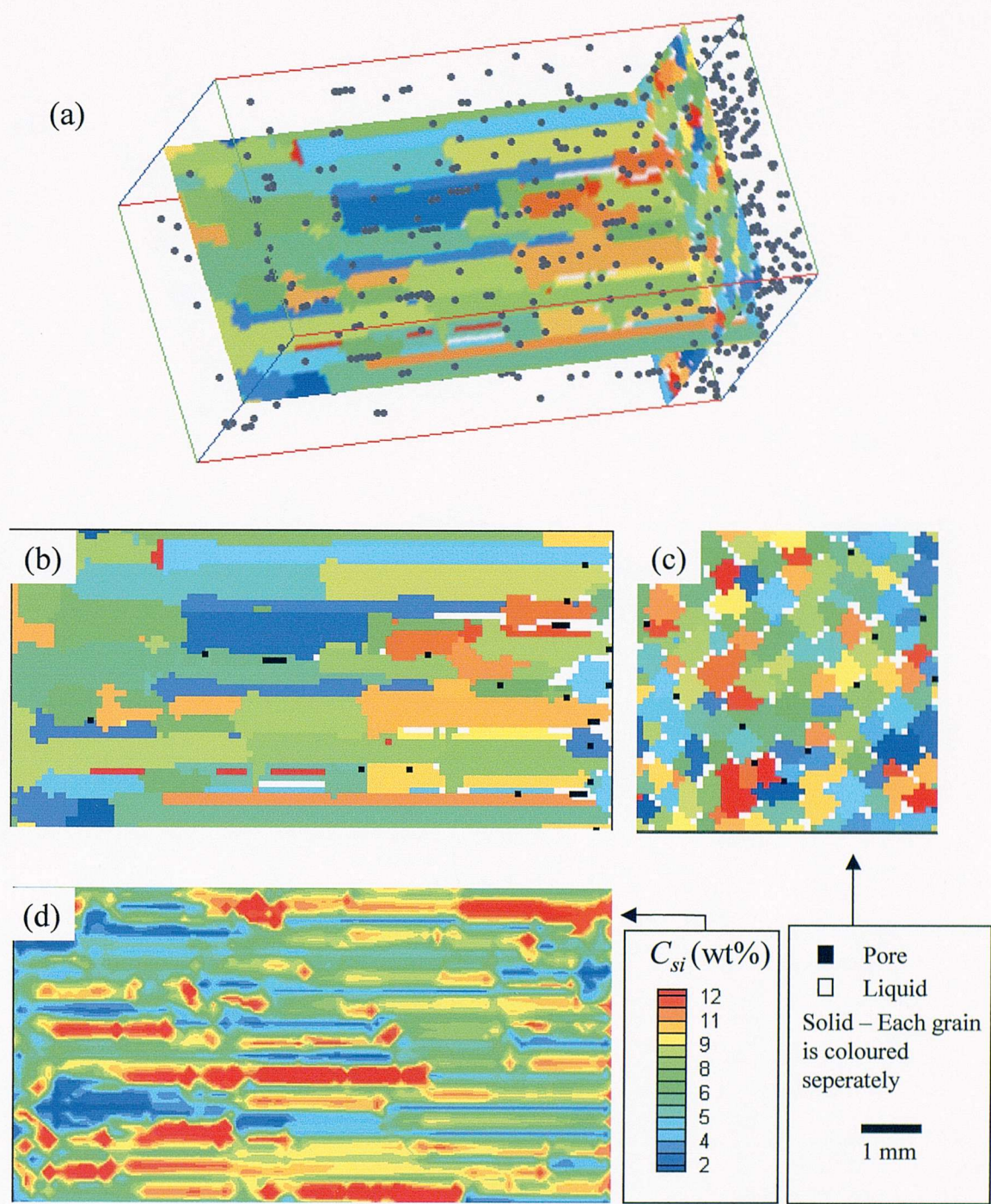


Figure 5-15. Directional solidification at $v=2\times10^{-4}$ m/s. (a) Three-dimensional image of the pores in the domain, with section planes indicated. (b) Image of the longitudinal section and (c) cross section, showing the grain structure and pores. (d) Longitudinal section showing the final segregation of silicon (the pores are omitted).

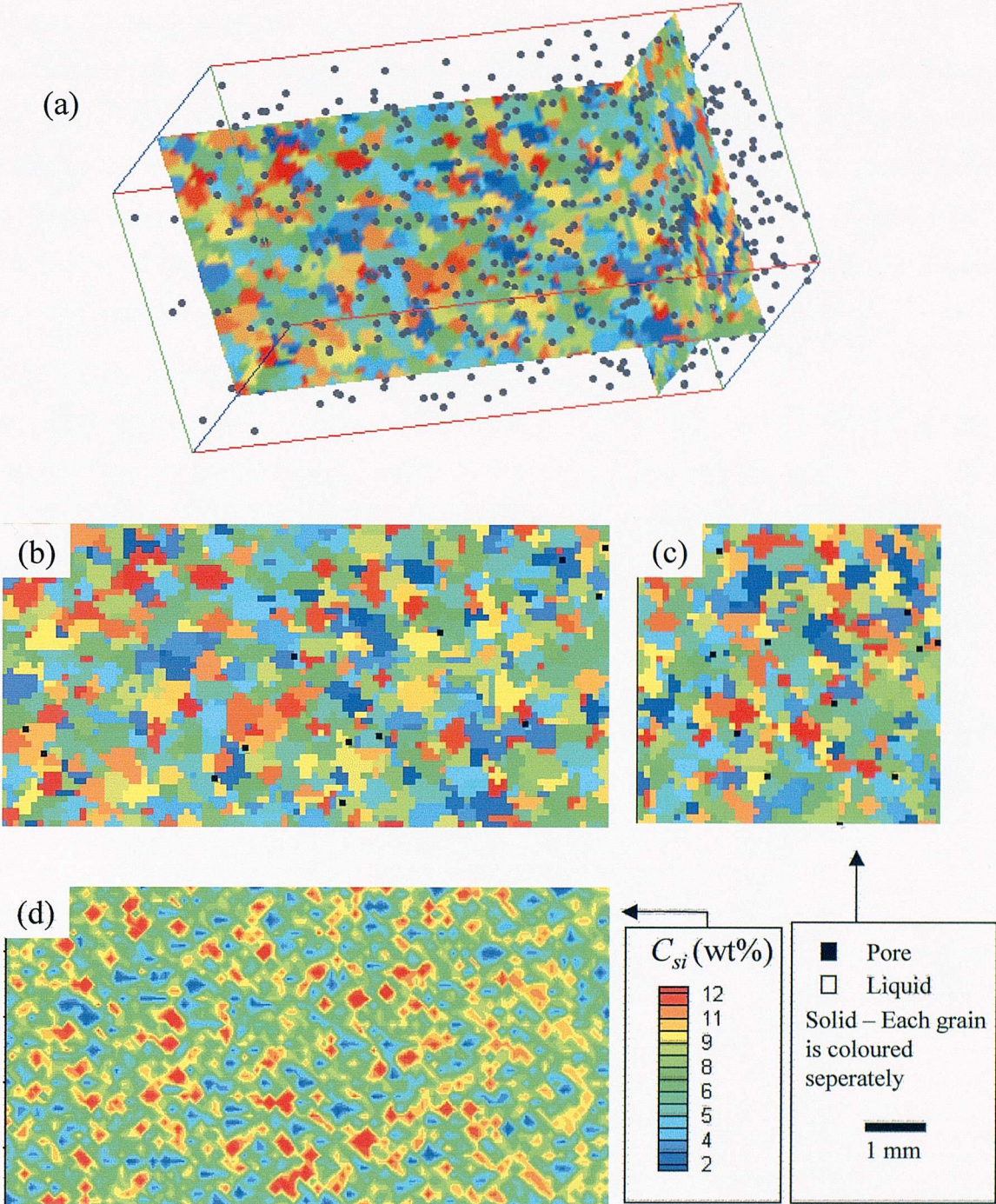


Figure 5-16. Directional solidification at $v=5 \times 10^{-4}$ m/s. (a) Three-dimensional image of the pores in the domain, with section planes indicated. (b) Image of the longitudinal section and (c) cross section, showing the grain structure and pores. (d) Longitudinal section showing the final segregation of silicon (the pores are omitted).

5.6. Factorial Analysis

These regimes of behaviour are not only dependent upon the solidification velocity. Other factors contribute to the balance of nucleation versus growth, and some of these factors and their interactions are studied in this section. The method of factorial analysis is used to determine the relative magnitude of the factor effects and their interactions. A full two-level four-factor design was used, with three repeats to estimate the statistical significance of these effects over the statistical noise. This required sixteen sets of parameters or 48 simulation runs for each experimental design.

5.6.1. Combined Solidification and Pore Parameter Effects

The effect of the microstructural development upon the final porosity in the model was examined by implementing a two-level full factorial experimental matrix for four factors: (a) N_n^G , (b) v_g , (c) C_H^i , and (d) N_n^p , which was analysed statistically [107] to determine the relative effect of each factor and the interactions among them on the porosity responses. The superscripts G for grain and p for pores are used to distinguish the respective nucleation densities N_n in this section.

The results are summarized in Table IX and given in greater detail in Appendix A. The arrows indicate the direction of change in the response (up or down) due to an increase in the factor.

Table IX. The most important factor effects. 1 wt% Si.

	I	II	III	IV
R_a	$v_g \downarrow$	$N_n^p \downarrow$	$N_n^G \uparrow$	$[N_n^G C_H^i] \uparrow$
L_m	$v_g \downarrow$	$C_H^i \uparrow$	$[v_g C_H^i] \downarrow$	
N_p	$C_H^i \uparrow$	$N_n^p \uparrow$	$N_n^G \downarrow$	$[N_n^G v_g] \downarrow$
P	$C_H^i \uparrow$	$v_g \downarrow$	$[v_g C_H^i] \downarrow$	$N_n^G \downarrow$

Table X. The most important factor effects. 7 wt% Si.

	I	II	III	IV
R_a	$N_n^p \downarrow$	$v_g \downarrow$	$C_H^i \uparrow$	$[N_n^G v_g] \uparrow$
L_m	$C_H^i \uparrow$	$v_g \downarrow$	$[v_g C_H^i] \downarrow$	
N_p	$C_H^i \uparrow$	$[v_g C_H^i] \uparrow$	$[N_n^G C_H^i] \downarrow$	$N_n^G \uparrow$
P	$C_H^i \uparrow$	$v_g \downarrow$	$N_n^G \uparrow$	$N_n^p \downarrow$

The factors are listed in order of decreasing magnitude.

Brackets [] indicate interaction factors.

At the 7 wt% level of silicon, the importance of the microstructural factors is generally reduced compared with the behaviour of the 1 wt% Si model. This results in v_g moving to

second place for the pore size responses R_a and L_m , and in N_n^P appearing as a factor for R_a and P . This is a result of the solute effect on the grain size; the difference in microstructure due to the change in v_g and N_n^G is less in the 7 wt% Si alloy than in the 1 wt% Si alloy.

The average pore radius is most sensitive to the imposed velocity v_g and the amount of pore nucleation N_n^P .

The maximum pore length predicted by the complex pore model is most sensitive to the imposed velocity v_g and the hydrogen content C_H^i . The interaction between these factors is also important. High v_g decreases the pore length, whereas high C_H^i increases it. However, the interaction effect is negative, indicating that at high velocities the effect of high hydrogen concentration is reduced. Only these factors appear statistically significant based on the three repeats of sixteen runs; the fourth-greatest factor was much smaller in its effect than these and so is not included in the table. See Appendix A for details.

The number density of pores per unit volume, N_p , appears to be sensitive to every factor and combinations of factors. However, this is most likely due to a violation of the assumptions which underlie the analysis – that the interactions are linear and that the populations are normally distributed. The most influential result is that when the factors v_g , C_H^i , and N_n^P are all at the high level, the number of pores increases by more than 100 times. Under these conditions, the high growth velocity results in liquid remaining at a greater undercooling, which in combination with high gas content and number of pore nucleation sites favours nucleation over growth and a large number of small pores form. This effect is so large as to not be properly explained by a linear model, which in this case tends to show statistical significance for all interactions.

The effect of grain nucleation is dominated by a particular interaction: when C_H^i is high, and v_g or N_n^P is high, low grain nucleation density results in a greater undercooling in the liquid, which is enough to trigger a large amount of pore nucleation thus resulting in a greater number of smaller pores with higher pressure gas within. Therefore, total pore volume is less than when the grain nucleation density is high. However, this is not significant if the gas level or velocity is low.

The effect of pore nucleation density is slight but seems counter-intuitive that increasing the pore nucleation should decrease the percentage of porosity. This may be explained similarly to the effect of grain nucleation: an increase in the number of pores results in less total volume, due to the higher pressure within each pore.

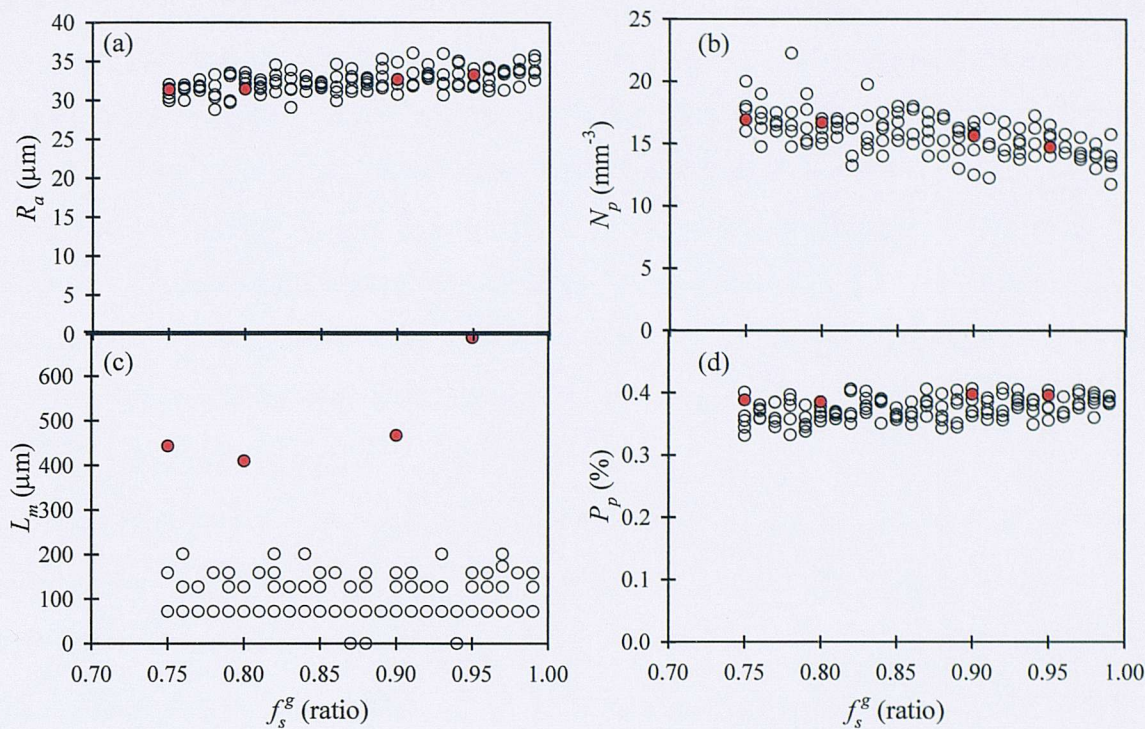


Figure 5-17. The effect of altering only the f_s^g ratio upon the porosity responses (a) average pore radius R_a , (b) maximum pore length (L_m), (c) pore number density N_p , and (d) percentage porosity P . The black symbols represent five repeats of 25 different values of f_s^g using 10x10x40 cell domains. The red symbols represent repeats with a larger model domain (3x in each dimension) which increases the overall maximum length observed but does not affect the averaged responses.

Table XI. The most important factor effects. 7 wt% Si.

	I	II	III	IV
R_a	$v_g \downarrow$	$A_\lambda \uparrow$	$G \downarrow$	$f_s^g \uparrow$
L_m	$v_g \downarrow$	$[v_g f_s^g] \uparrow$	$[v_g C_H^i] \downarrow$	
N_p	$v_g \uparrow$	$G \uparrow$	$[v_g A_\lambda] \uparrow$	$[v_g G] \downarrow$
P	$v_g \downarrow$	$A_\lambda \uparrow$	$f_s^g \uparrow$	$G \uparrow$

The factors are listed in order of decreasing magnitude.

Brackets $[]$ indicate interaction factors.

The necessity of including the approximation described in Section 4.1.5 for stabilizing the solid phase growth does not have a significant effect upon the porosity size responses. There is a slight but noticeable negative effect upon the number of pores, if f_s^g is varied alone. Figure 5-17 shows the results of five repeats of 25 levels of f_s^g and show that the variation in the average and maximum pore dimensions R_a and L_m is mostly random. Trebling the model domain in each dimension (red points) certainly has an effect upon the overall maximum pore length (Figure 5-17(c)) because the smaller system size limits the growth of the largest pores, but the effect on the system wide properties as shown in the other graphs of Figure 5-17 cannot be distinguished from the variability.

Since f_s^g is varied for a constant grid dimension, the effect on porosity of the residual dependence upon the grid dimension of the solidification microstructure results in the slight dependence of the porosity upon f_s^g .

5.6.2. Growth and model effects

The effects of varying the growth parameters were also studied by a four-factor experiment, in which the velocity v_g , thermal gradient G , growth threshold f_s^g and the spacing factor A_λ were varied independently. The results show that among these v_g and A_λ are the most significant factors affecting pore size with the effect of v_g being the greatest. The results are summarized, in decreasing order of magnitude, in Table XI, and given in more detail in Appendix A.

5.7. Bubble Surface Model

In this section, the equilibrium configuration for some approximations to the system of a gas bubble within a dendritic network of solid and liquid are determined, using the surface evolver model [103]. The model predicts the equilibrium configuration; to determine the volume and pressure expected in a slowly growing bubble, the amount of gas was increased by small amounts and the equilibrium determined at each step, in order to compare the more accurate predictions available by this method, which includes the three-dimensional shape without any assumption of cylindrical symmetry, with the approximation described in Chapter 3. The surface simulations were all carried out on $1/4$ of the domain by assuming reflective symmetry at the x and y axes, so the possibility of such a bubble asymmetrically adhering to one of the solid rods was not considered.

5.7.1. Single Bubble

The minimum energy configuration for a single bubble determined by the finite-element minimisation model including the compression energy under the ideal gas law assumption,

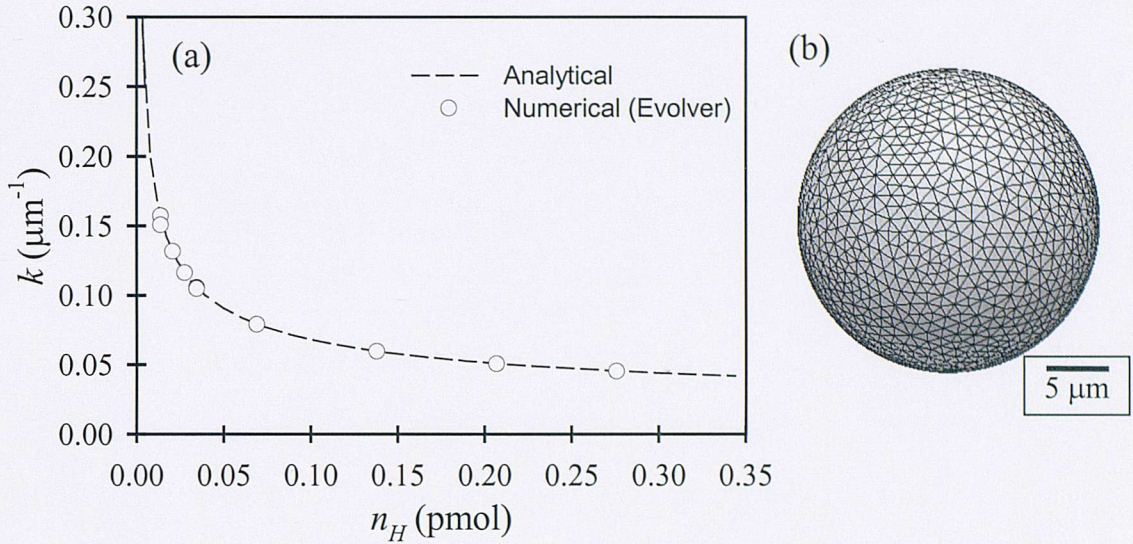


Figure 5-18. (a) The dependence of the volume of an isolated bubble upon the amount of gas in the bubble, as predicted by the finite-element energy minimization model (using the Surface Evolver [103]) compared with the analytical formulation Equation 2-31a. (b) An image of the resulting configuration containing 0.07 pmol of gas. The bubble is spherical as expected.

gives the result shown in Figure 5-18 (a) for the case of an isolated bubble. The dependence of the volume upon the amount of gas agrees with the analytical solution, given by Equation 2-31a and also plotted on the graph. The shape is shown in Figure 5-18 (b) and is the triangulated approximation to a sphere, as predicted by theory.

5.7.2. Constrained Bubble Interaction with Surface

Applying a constraint consisting of four parallel right circular cylinder surfaces spaced $10 \mu\text{m}$ apart results in the relationships shown in Figure 5-19, and the shape of the bubble is shown in Figure 5-20 for a high- γ_{sg} and a low- γ_{sg} case. The relationship predicted by the assumption used in the curvature-limited pore model. Equation 3-26 predicts horizontal lines – constant curvature if f_s is constant and only n_H changes. This approximation is qualitatively appropriate but requires a constant that depends upon the surface tension γ_{sg} . The two-dimensional reasoning described in Section 3.2.4 breaks down somewhat for the case where the contact angle is 90° , since the curvature for the 2d case (or a cylindrically symmetrical case) should be zero whereas for the four-rod case the mean curvature is not zero. However, the curves representing the different fraction solid (determined by the rod radius r_r) approach one another, and when the contact angle is greater than 90° , their relative position is inverted – the pressure decreases for increasing f_s though the calculated curvature is not always negative, as the axi-symmetrical case would predict. For the four-rod case, f_s has been determined using Eqn. 5.5 below.

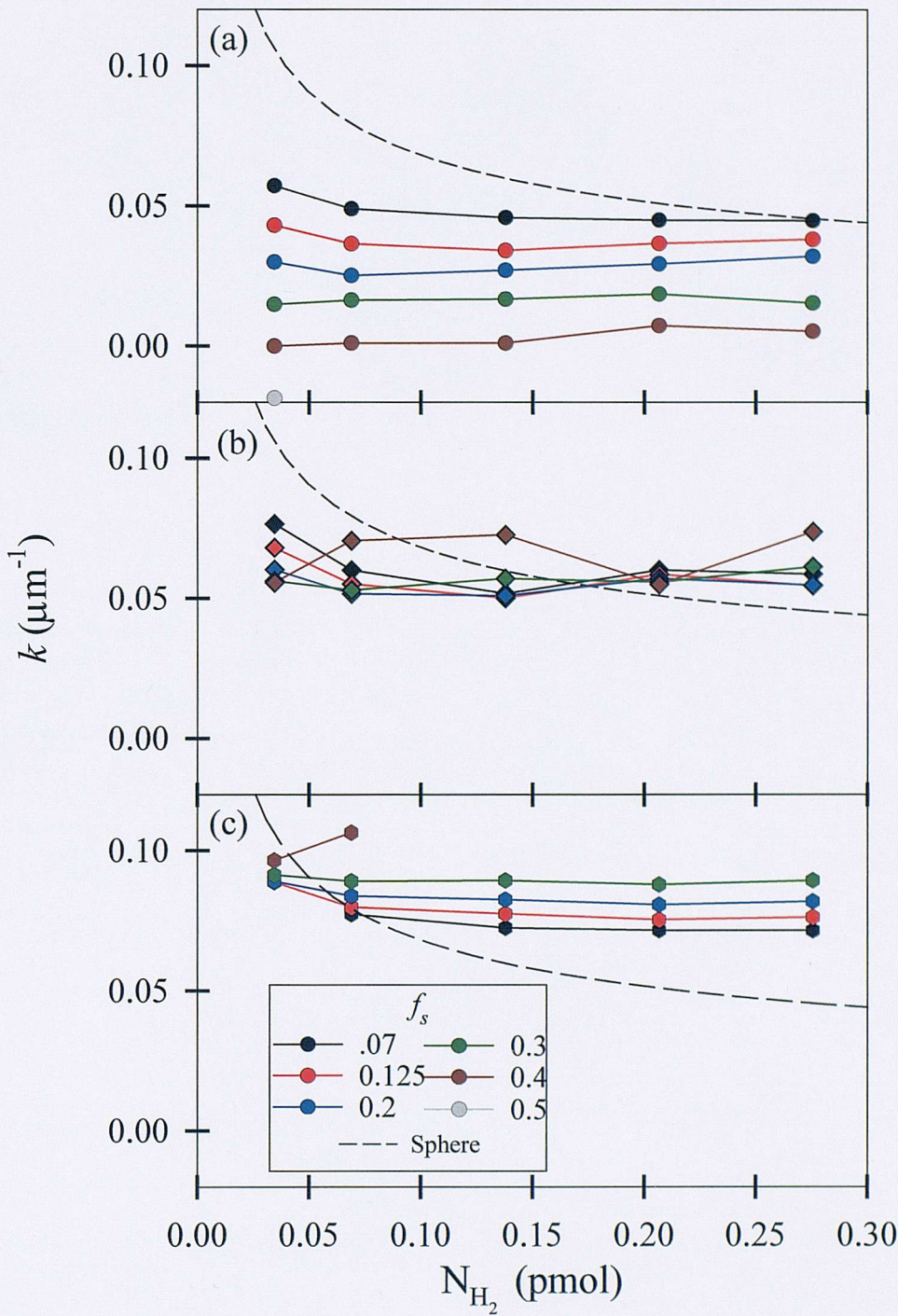


Figure 5-19. The relationship between the amount of gas n in a bubble and the mean curvature k , for a bubble trapped between four rods, for various values of the fraction solid, plotted for different values of the surface tension contact angle θ : (a) $\cos\theta = -0.5$ (b) $\cos\theta = 0$ (c) $\cos\theta = 0.5$ The relationship for a sphere is superimposed.

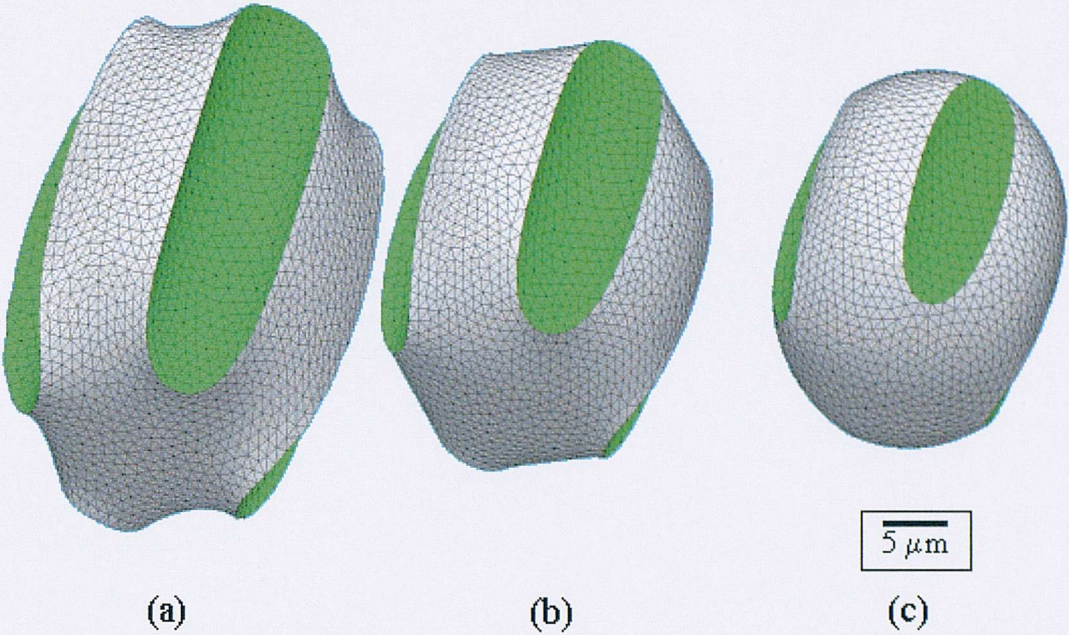


Figure 5-20 Calculated shapes for a bubble containing 0.07 pmol of gas, trapped between four rods with $r_r=5\mu\text{m}$ and $\lambda_r=10\mu\text{m}$ for three values of the contact angle θ : (a) $\theta = 120^\circ$ ($\cos\theta = -0.5$), (b) $\theta = 90^\circ$ ($\cos\theta = 0$) and (c) $\theta = 60^\circ$ ($\cos\theta = 0.5$). The gas-solid interface elements are green and the gas-liquid interface elements are white.

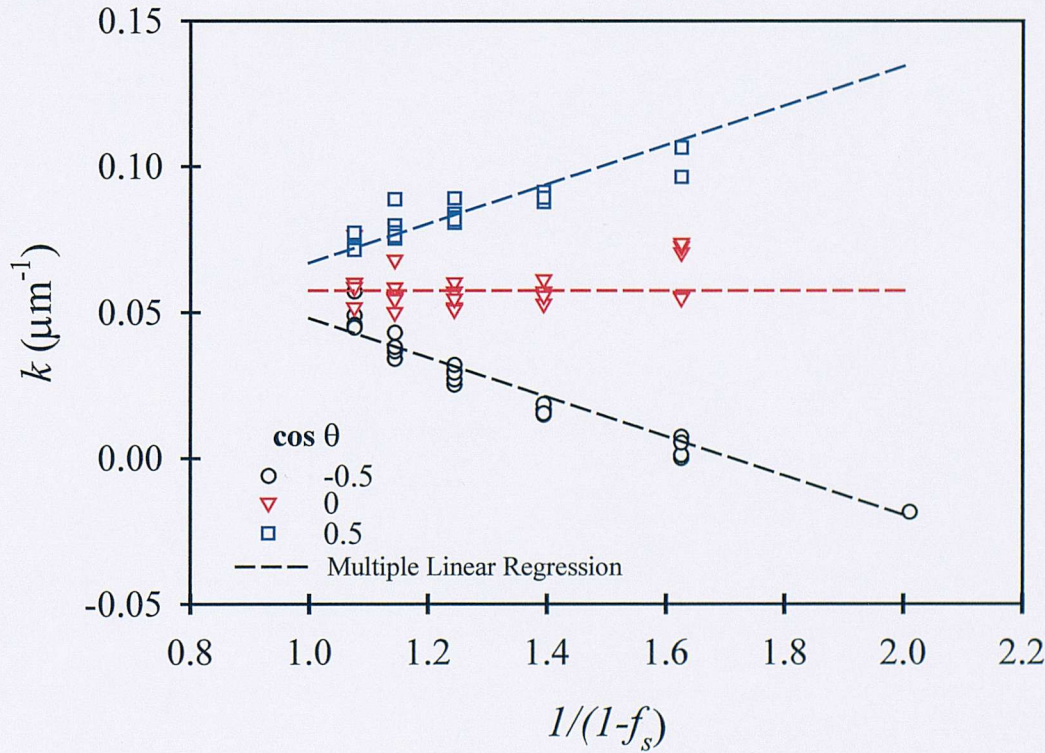


Figure 5-21. The curvature k as a function of calculated f_s for the bubble surface and rods model for different surface contact angles, pooling the results for varied n_{gas} .

The mean curvature $\bar{k} = 1/r$ as calculated from the equilibrium pressure:

$$\bar{k} = \frac{\Pi - \Pi_a}{2\gamma_{lg}} \quad (5-3)$$

as a function of total amount of gas in the bubble is shown in Figure 5-21 for a several values of the rod diameter and the contact angle θ ,

$$\cos \theta = \frac{\gamma_{sg} - \gamma_{ls}}{\gamma_{gl}}, \quad (5-4)$$

with a constant rod spacing $\lambda_r = 20 \mu\text{m}$ and $\gamma_{lg} = 0.865 \text{ N/m}$. An increase in the rod diameter corresponds to an increase in the fraction solid according to the approximation used, which gives the geometrical relationship:

$$f_s = \pi \left(\frac{r_r}{\lambda_r} \right)^2 \quad (5-5)$$

in which λ_r was kept constant at $20 \mu\text{m}$ and the rod radius r_r was varied from 3 to $8 \mu\text{m}$.

Figure 5-20 shows the resulting bubble shapes for $r_r = 5 \mu\text{m}$ with the different surface energy settings but a constant amount of gas $n_{\text{gas}} = 0.07 \text{ pmol}$; the bubble becomes significantly larger when the solid-gas surface energy is lower or rather when the ratio of equation 5-4 is low.

The correspondence with the assumption of Section 3.2.4 is quite good except an additional factor should be added. A multiple linear regression fit of the results shown in Figure 5-19 yields the equation:

$$\bar{k} = 0.057 - 0.116 \cos \theta + 0.135 \frac{\cos \theta}{(1 - f_s)} \quad (5-6)$$

with very good statistical significance ($R^2 = .953$, $P_i < 0.01$). Including the amount of gas in the regression for the curvature did not show significance by itself or as an interaction with the $\cos \theta$ or $(1/f_i)$ terms, qualitatively supporting the curvature limiting assumption. The results of equation 5-6 and the simulation are shown in figure 5-21.

If the liquid wets the solid quite poorly, *i.e.* if $\gamma_{sg} < \gamma_{sl}$ then the relationship between the pressure and the rod diameter is reversed. In this case, the pressure in the bubble becomes lower as the rods increase in size indicating that in this situation, a pore in a casting would

expand dramatically as the fraction solid increases if the surrounding liquid is free to move away.

The relationship shown could be included into the pore size calculations, though the true geometry of the dendrites is only very roughly approximated by the four cylindrical rods. Applying a version of the finite-element surface-minimization routines for each bubble, responding to its actual surroundings in the simulation, would be feasible only for a very few bubbles at a time but should be possible.

6. APPLICATION: AL-SI

In this chapter, the model is used to compare with experiments on Al 7wt% Si alloy, considered also to be a reasonable approximation to the A356 alloy used in some of the experiments. The spherical approximation to the pore shape was used in this work. It is shown that the spherical assumption produced valid results for this system. Examination of the sources of systematic error led to the development of the complex pore model.

Laboratory experiments of Lee and Hunt [110] in which the growth of pores were observed directly during solidification in an X-ray temperature gradient stage microscope (XTGS), controlled castings of Fang *et al.* [29, 56] and industrial survey experiments of Tynelius *et al.* [29] were used for comparison of the porosity predictions, and a wedge casting [109] was used as an exercise aimed at combining commercial macro-modelling of heat transfer with the micro-modelling of the grain and pore structure.

The model was validated by varying the solidification time, t_s , and the initial hydrogen content, C_H^i , to compare with prior results. The sensitivity was studied by varying the total number of potential nuclei, N_n , and the minimum nucleation threshold, s_{min} . Interactions between C_H^i , and t_s and between C_H^i , and N_n were studied by using a range of values for each parameter. By covering a range of conditions of C_H^i , and t_s , constitutive equations were developed to enable the application to castings of a larger size than may be feasibly discretised at the $10^{-5} - 10^{-4}$ m scale suitable for modelling the microstructure. These equations were applied to the results of modelling the thermal history of the test wedge.

6.1. Comparison with Experiments

The model predicts a detailed structure for the solidifying melt as seen in Figure 6-1. The grains are shown as semi-transparent isosurfaces at 90% solid and the pores are shown as darker spheres. The complicated three-phase structure is modelled in three dimensions including the variation in the concentration of the dissolved elements. In the illustrated case, a temperature gradient was applied and translated along the model domain. Figure 6-1(a) shows the structure at an earlier time than Figure 6-1(b). Areas that are fully solid or fully liquid are rendered completely transparent. The concentration of dissolved Si in the liquid exhibits enrichment around growing grains, as shown in Figure 6-2(a) and the supersaturation of dissolved H exhibits enrichment around growing grains and depletion around pores, as shown in Figure 6-2(b).

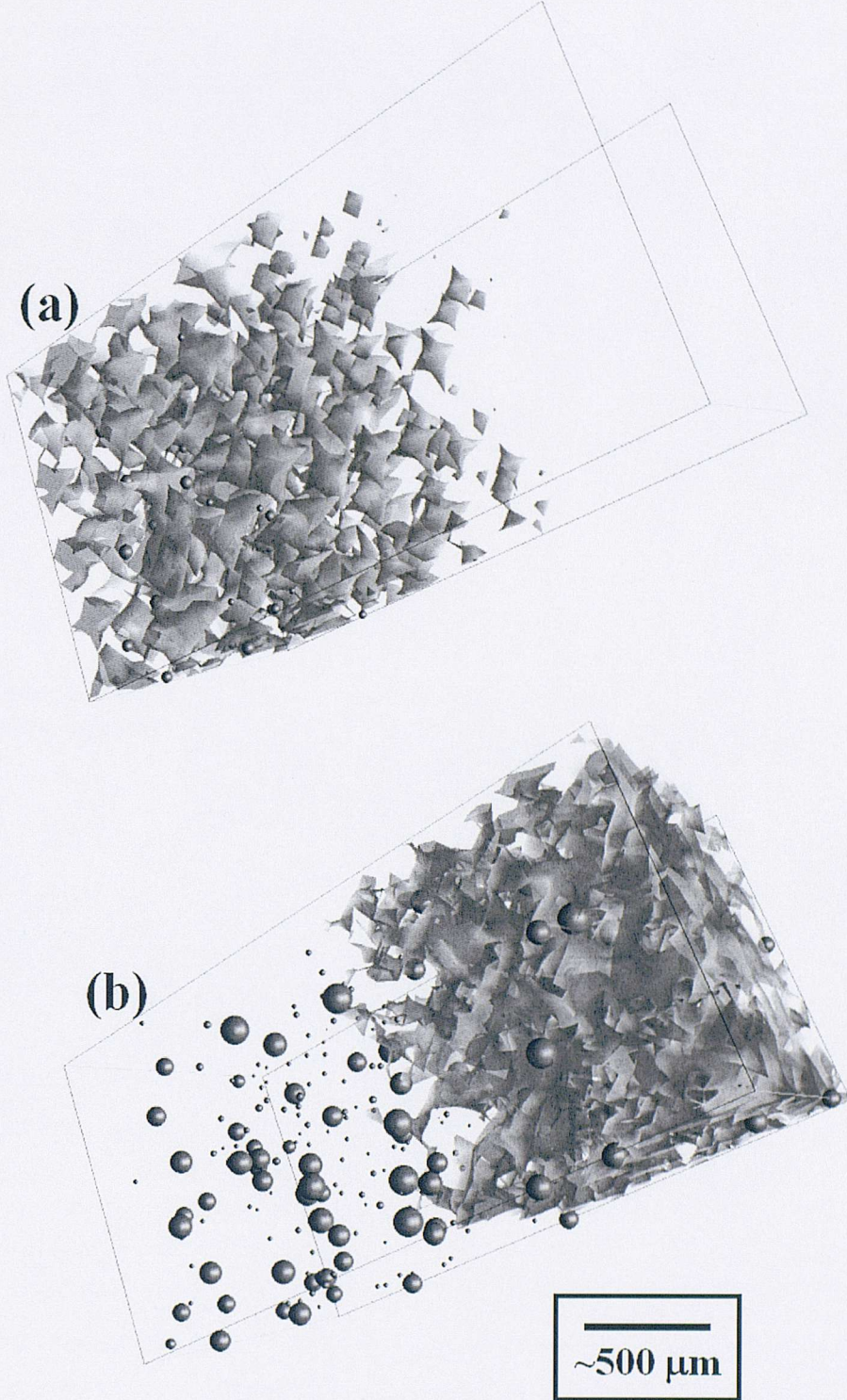


Figure 6-1. A three-dimensional perspective view of a partly solidified model domain shown (a) when the start-of-freeze has passed partly through the domain; and (b) when the end-of-freeze has passed partly through the domain. The isosurface at 90% phase has been rendered partly transparent so that the bubbles may be seen.

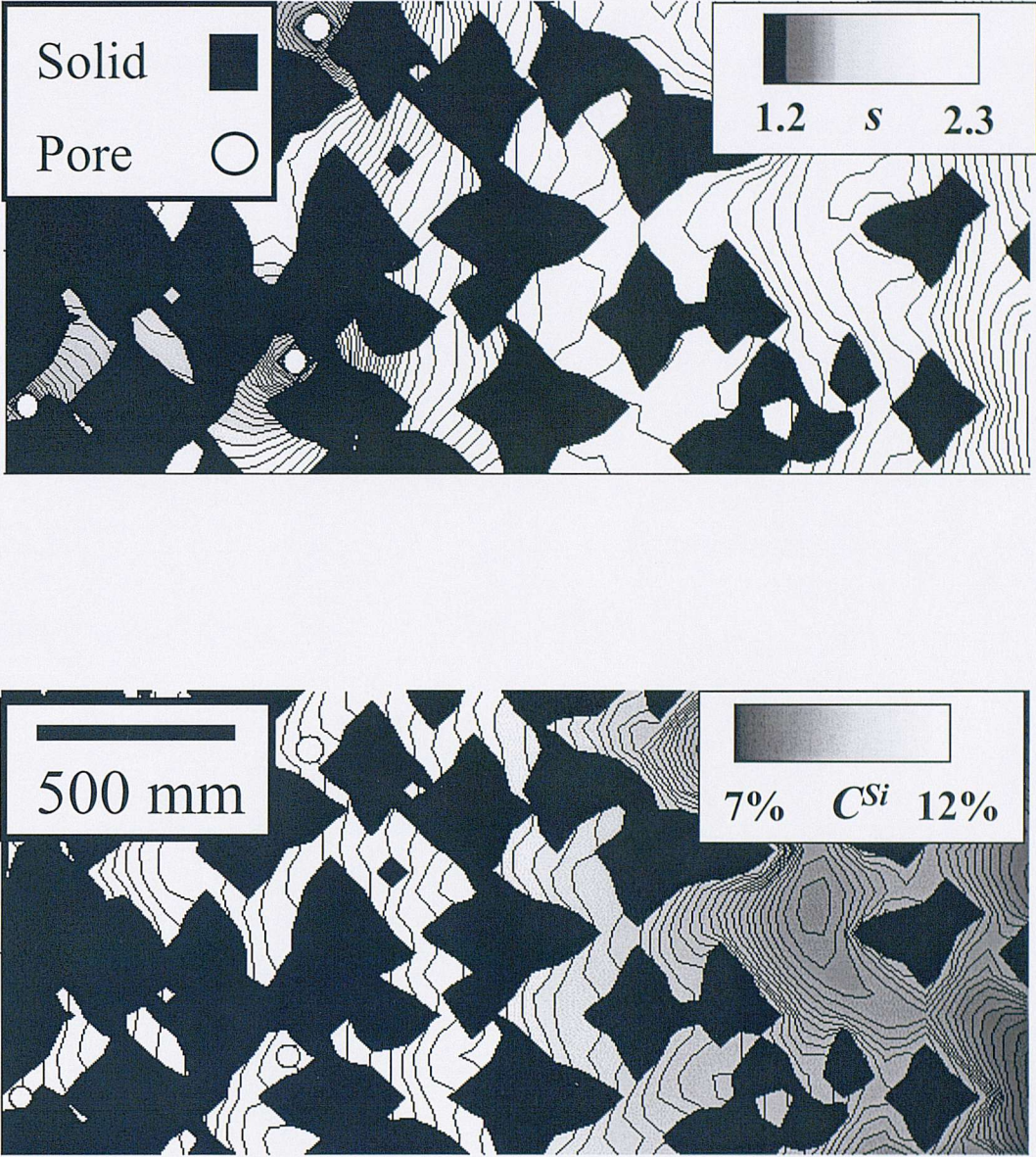


Figure 6-2. Two-dimensional slices of a directional solidification simulation with contour maps of (a) the hydrogen supersaturation s and (b) the silicon concentration C^{Si} .

Each pore has unique surroundings and history. The shape of the nearby grains creates a twisting network of liquid channels (as seen in Figures 6-1 and 6-2) which determines the rate at which hydrogen can be transported, the growth of the grains determines the amount of hydrogen present due to segregation, the temperature and Si concentration determine how much may be dissolved, and the dissolved Si causes the metal to remain liquid at lower temperatures. Furthermore, each pore depletes the hydrogen in the surrounding area, so the distance to other pores in the domain also affects the amount of hydrogen available. The relative magnitude of these effects on each pore is predicted by the simulation, and the average response and the range of response within a population of pores is determined.

The XTGS experiments allow comparison of the simulated pore growth with the observed growth of individual pores. The graphs in Figure 6-3(a) show the radius-temperature profiles for several pores, compared to similar results from a model run in Figure 6-3(c). In each case the growth curves show an initial rapid increase in the radius with the rate of increase falling off as the pore grows.

The nucleation temperature histogram for the model is shown in Figure 6-3(d). In order to compare with the experimental results, Figure 6-3(b), the temperature domain has been divided into 2°C bins as was done for the experiments [110]. Despite the very simple ‘step’ distribution used for the nucleation in the model, the nucleation histogram shows a good qualitative similarity with that from the experiment, resulting in a peaked distribution.

Gaussian curves of the form $y = a \exp(\frac{x - \bar{x}}{\sigma})$ were fitted to the histograms in Figure 6-3, and the parameters for the fitted curves are given in Table XII.

Table XII		Parameters for Gaussian Fit	
	Model	Exp	Units
$\bar{x}$	604	609	°C
σ	3.8	2.3	°C
a	10.9	11.3	N

In the XTGS experiments, G was maintained constant within each run and as nearly constant as possible between runs, and v was maintained constant within each run. Thus t_s could be characterized by $(T_{liq} - T_{sol})/(Gv)$ for each experiment. To simulate these situations, G was maintained constant at 6.3 K/mm while v was varied in the model. The results are shown in Figure 6-4.

The model tracks the amount of gas and the equivalent spherical radius of each activated pore for the duration of the model run. For clarity in the figures, only a dozen pore traces are shown out of around 200 that were recorded or simulated; those selected include the extremes. The growth of each pore is characterized by a sharp initial increase in radius. Subsequently the rate of growth gradually decreases as the sphere expands, as hydrogen concentration declines in the liquid, and as the diffusion coefficient decreases. Some of the curves increase more rapidly than others due to differing local environments and interaction of the diffusion fields of neighbouring pores.

These effects combine to decrease the growth rate when compared with the analytical solutions which assume constant diffusion and an infinite domain. If a power law relationship

is fitted to each pore radius as a function of time elapsed from its nucleation, the resulting exponents range from 0.30 to 0.45, compared to 0.5 for the ideal case described by Equation 2-32. The effects of restriction of the diffusion path as the solid forms, the decrease of diffusion coefficient as the temperature decreases, and most importantly the sinking of hydrogen into other nearby pores combine to progressively decrease the amount of hydrogen entering the pore and lower the apparent growth exponent. The increase in growth rate due to the increase in C_H resulting from H segregation is not sufficient to offset these effects.

The main effect of increasing the amount of hydrogen available, Figure 6-5, is to increase the size and number of pores, which combine to cause an increase in the final percentage porosity. This agrees with the well-known effect [4] of increasing hydrogen in Al castings, as reported quantitatively by Fang *et al.* [56]. The number of pores also increases, albeit with significant scatter due to the stochastic nature of the nucleation model.

The stochastic nature of the placement of grain and pore nuclei gives rise to the spread of results as shown in Chapter 5, Table VII, which represents the results of changing only the location of the potential nuclei. The magnitude of this effect upon the final porosity responses relative to the effect of changes in t_s and C_H^i can be seen in Figures 6-4 and 6-5 where the trend due to the parameter variation is clearly visible, but noticeable random variation is superimposed.

This prediction of the behaviour of an entire population of pores, rather than an individual pore, allows the application of statistical methods to the results, for example, the prediction of the response surface by multiple linear regression as discussed below. The effect of varying t_s and C_H^i on the maximum radius is shown along with the average in Figures 6-4(a) and 6-5(a). The maximum will also depend upon the initial distribution of nuclei, as is shown by the results due to random configurations shown in Chapter 5, Table VII. The range of the maximum radius results over the 50 simulations ran from 85.5 to 117.7 μm . Since the largest defect in a critical region will determine the fatigue behaviour, this type of prediction is useful.

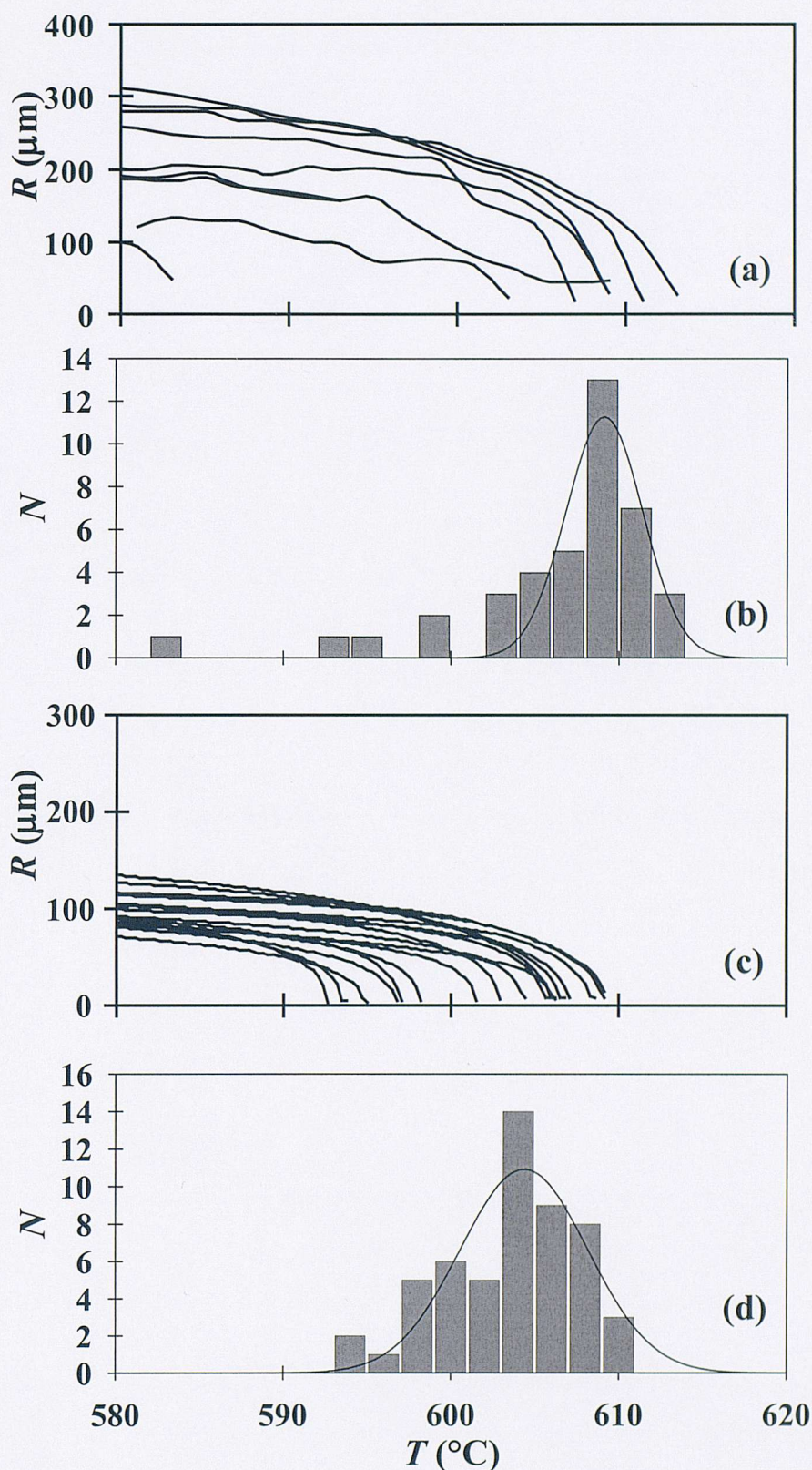


Figure 6-3. Typical results from XTGS characterisation of pore growth: (a) the growth of individual pores, (b) histogram of the nucleation temperature of all pores observed (Source: Lee [110]); and results from the CA simulation of pore growth: (c) the growth of individual pores, (d) histogram of the nucleation temperature of all pores.

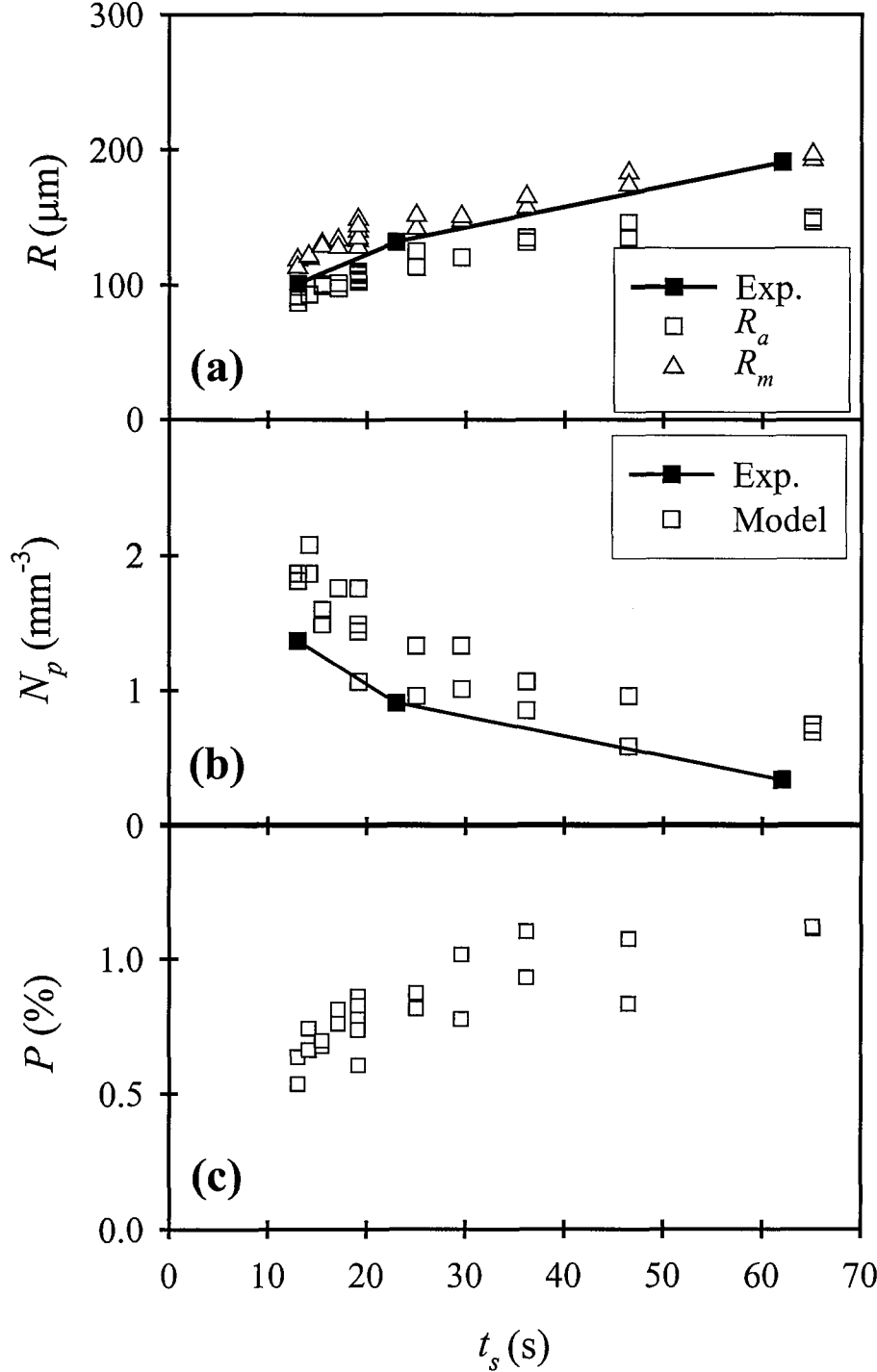


Figure 6-4. The effect of changing the directional solidification velocity on (a) the maximum and average pore radius, (b) the pore number density, and (c) the percentage porosity. The results are plotted against the local solidification time; all runs used a gradient of 6300 °C/m.

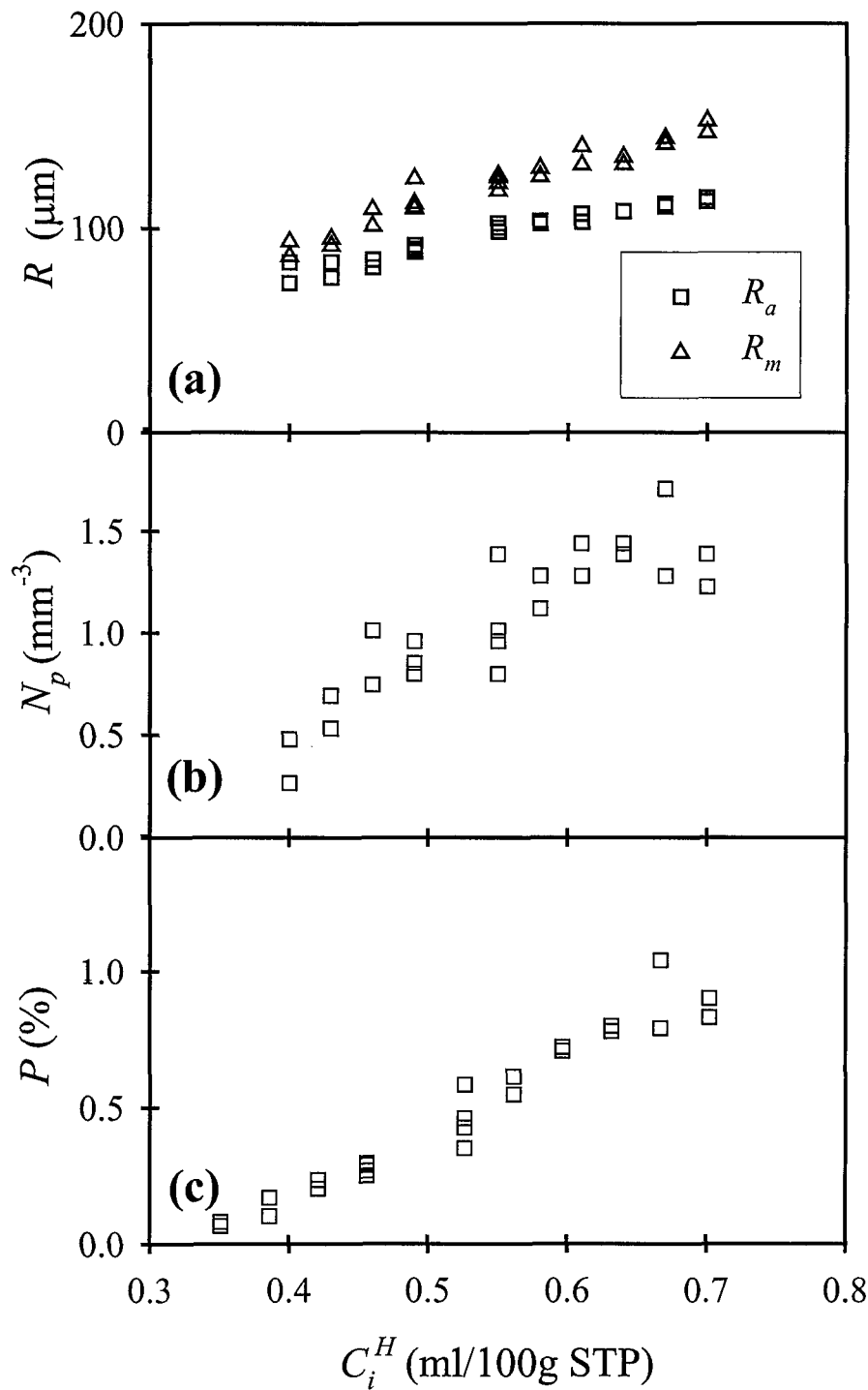


Figure 6-5. The effect of changing the initial hydrogen concentration on (a) the maximum and average pore radius, (b) the pore number density, and (c) the percentage porosity.

The stochastic nature of the nucleation processes also affects the apparent nucleation distribution. In the XTGS experiments, the nucleation temperature for each pore was measured, resulting in histograms as shown in Figure 6-3(b). The model assumption that the nucleation depends upon the supersaturation results in the histogram of nucleation events shown in Figure 6-6 when a sharp step distribution of nucleation probability over supersaturation (dotted) is used as the input. When the simulation cell temperature at which the nucleation occurred is used for the histogram, the result shows a good similarity to the experimental histogram as seen in Figure 6-3(d). The differences in the pore surroundings combine to produce a spread in the temperature at which a given degree of supersaturation is reached, altering the simple step into a smoothly varying peak resembling a bell curve.

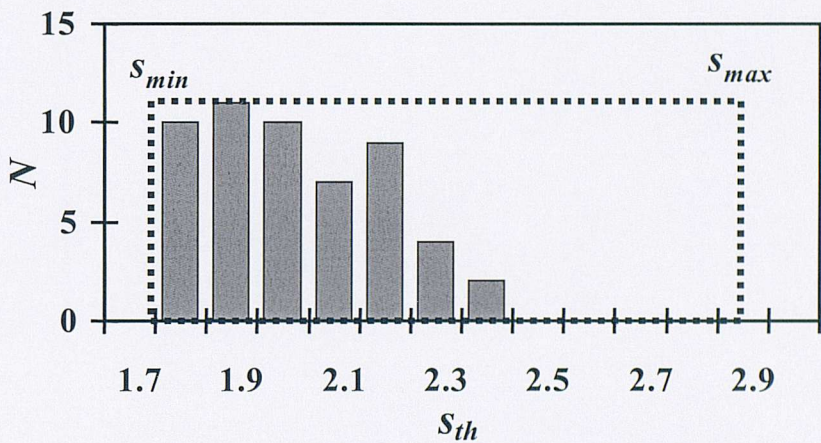


Figure 6-6. Histogram of the nucleation supersaturation of all pores.

Fang *et al.* [56] experimentally measured the effects of varying C_H^i and t_s upon porosity responses. The model was run using their ranges of experimental conditions and the results are plotted in Figure 6-7 along with their results.

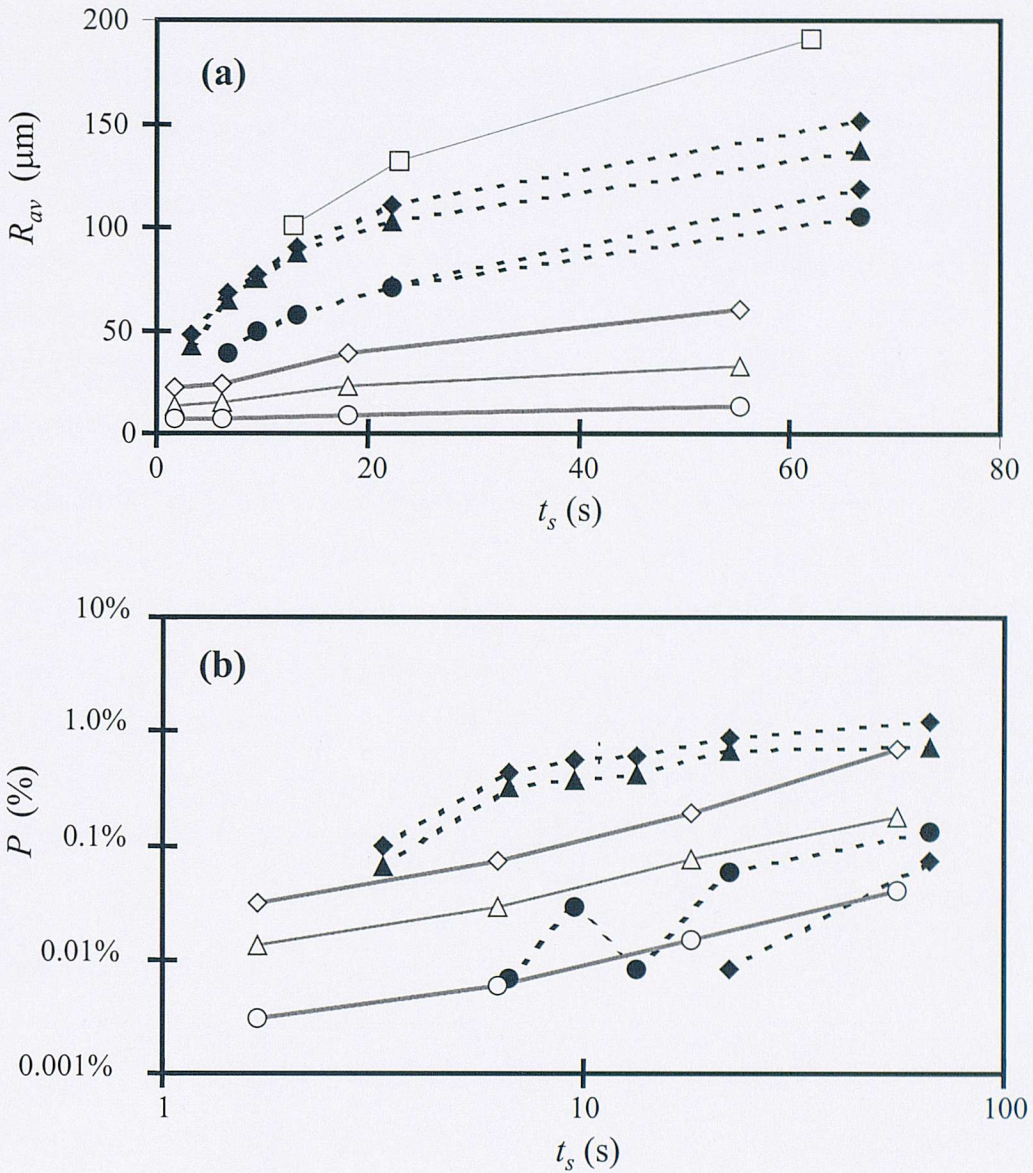


Figure 6-7 Comparison of the model results (solid symbols) to the experiments of Fang *et al.* [56] (hollow symbols) for (a) R_a and (b) P . The initial hydrogen concentration (in ml/100g STP) was: $\blacklozenge$ 0.45; $\blacktriangle$ 0.41; $\bullet$ 0.25; $\blacklozenge$ 0.2; $\diamond$ 0.31; $\triangle$ 0.25; $\circ$ 0.13; $\square$ 0.26.

It was found that increasing both N_n and s_{min} gave better correspondence with the results of Fang *et al.* This indicates that the alloys used in the XTGS experiments may have contained nucleating agents for the pores which were more effective than those in the alloy used by Fang *et al.* but fewer in number. Such heteronuclei would cause the pores to nucleate at a higher temperature, and the neighbourhood of each pore would have a lower fraction of solid.

The composition of the A356 alloy used by Fang *et al.* contains 0.41% Mg whereas the XTGS experiments used the pure binary Al7Si and hence the freezing range is extended and H

solubility increased [42]. This allows the pores to continue growing for a longer time but could allow more H to remain in solution. However, this amount of Mg is quite small relative to the actual H concentration present, so these effects should be minor.

Measuring the porosity by the X-ray technique gives the full extent of pores whereas metallographic sections may have intersected a pore more than once, resulting in a smaller size measurement and greater number count, though the total volume fraction would be accurate [117]. However, the typical micrographs shown in reference [56] appear to have separated, rounded pores.

A further difference between the model prediction and the experiments could be due to the effect of the impingement of the pore upon the solid around it, which would tend to restrict the growth of the pore. This would increase its surface curvature and hence its internal pressure (as given by Equation 3-18). This effect would be more significant if the pores nucleate when the alloy is more fully solidified. This could explain why the results of Fang *et al.* show smaller pores than the model predicts. The complex pore growth model, including such restrictions, was developed subsequently in order to address this issue.

Tynelius *et al.* [29] generated process maps by experimentally measuring the pore number density resulting from different values of t_s and C_H^i , then applying multiple linear regression to the results. Their contour plot of the response surface is shown in Figure 6-8(a). A process map from the model comprising a multiple linear regression fit to the results of 10 values each of t_s and C_H^i is shown in Figure 6-8 (b).

Within the range here studied, the qualitative agreement with the model predictions (shown in Figure 6-8(b)) is good, and reproduces the observed behaviour, that the pore number density increases with gas content at low solidification times and decreases with gas content at high solidification times. The predicted number density was modelled by a relationship of the form:

$$N_p = A_0 + A_1 \log t_s + A_2 C_i^H + A_3 C_i^H \log t_s, \quad (6-1)$$

where the parameters A_i and the statistical significance indicators are given in Table XIII.

At low concentration of hydrogen, an increase in solidification time causes an increase in the number of pores. In this regime, the coupling between the solidification and the pore nucleation dominates. If the solid does not grow fast enough, the locally segregated hydrogen diffuses away and the degree of supersaturation is less likely to reach a level allowing

nucleation of a pore. With greater amounts of hydrogen, the supersaturation level becomes high enough to allow nucleation even if diffusion equilibrates the concentration throughout the liquid. Increasing the solidification time then allows more time for early nucleating pores to sink hydrogen, resulting in fewer pores. This important interaction between hydrogen content and solidification time upon the pore number density shown by the statistical analysis of [29] is qualitatively reproduced by this model.

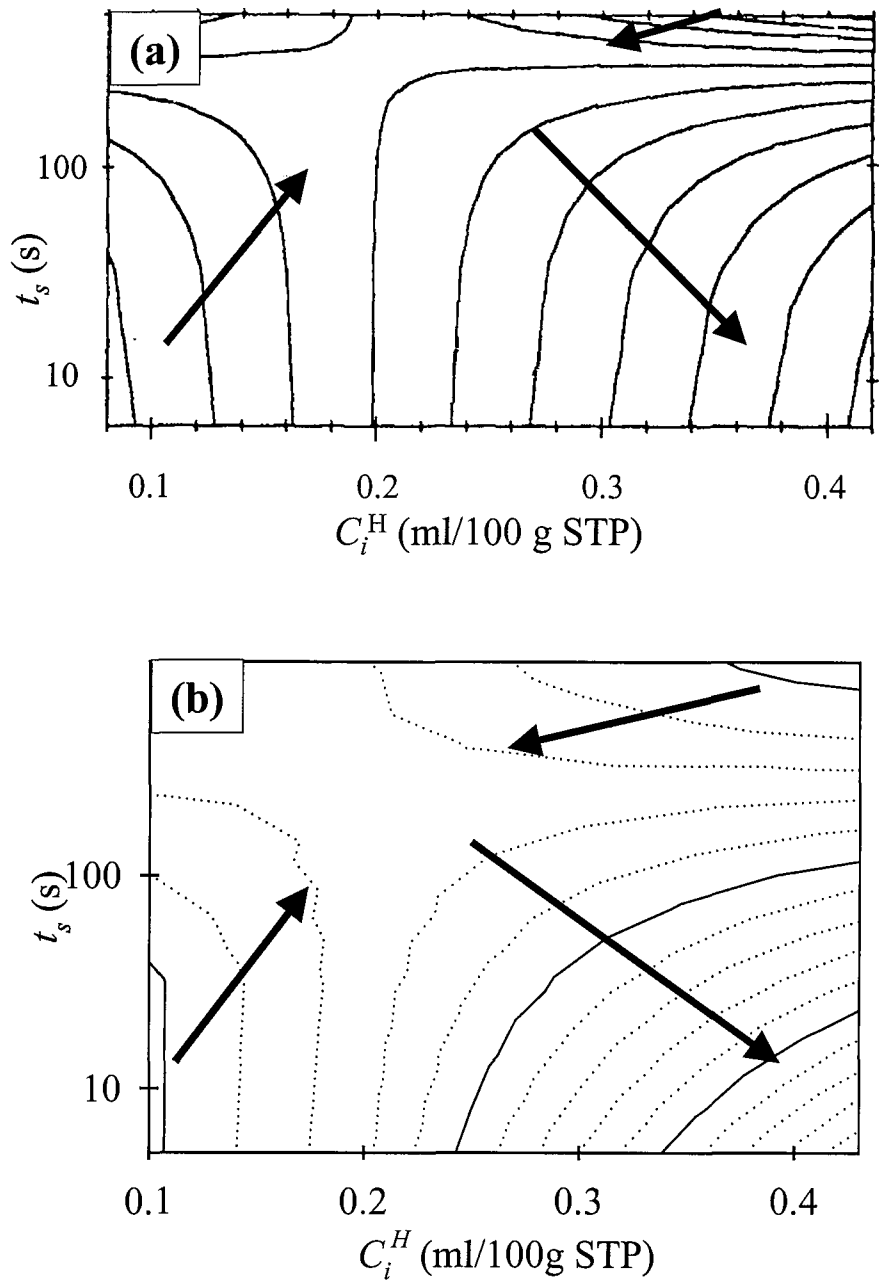


Figure 6-8 Qualitative comparison of (a) the results of Tynelius *et al.* [29] for area pore number density with (b) the results of the model for volume pore number density, shown as contours in a V - C_H^i plane. (The arrows indicate directions of increasing pore numbers.)

Table XIII. Regression results for N_p .
 $N_p = A_0 + A_1 \log t_s + A_2 C_H^i + A_3 C_H^i \log t_s$;
 $R^2 = 0.915, F = 246$

Coefficient	Value	P value
A_0	-57	1.3e-06
A_1	28	1.8e-06
A_2	364	9.3e-20
A_3	-148	2.1e-15

Although the number density in the model results shows a considerable range, bracketing the experimental results at least for the two faster velocity XTGS experiments, the pore size is smaller than the experimental pore size in these experiments, and using an initial hydrogen concentration significantly greater than that measured in the experimental melt gave better results than did the measured concentration. This difference cannot be explained by nucleation mechanisms. Possible reasons for inaccuracy in the model are:

- that the inaccuracy due to the pore size exceeding the cell size systematically inhibits the growth of large pores,
- that the formulae for the solubility and diffusion of hydrogen in the aluminium are not accurate within the mushy zone,

moreover, some experimental error might have occurred due to:

- the hydrogen content not remaining at the initial level during the entire experiment,
- the pressure reduction due to shrinkage was greater than previously supposed.

The third point above is particularly likely since the XTGS samples needed to be very thin to allow the passage of sufficient X-rays to resolve the pores, therefore the ratio of surface area to volume was very large. This likely exacerbated the absorption of atmospheric moisture after the time of measurement from the crucible and during the experiment. The final samples were too small to obtain useful hydrogen measurements from. However, the presence of this effect does not exclude the other mentioned effects.

6.2. Sensitivity to Nucleation Parameters

If the input number density is varied, Figure 6-9, the final pore number density, N_p , varies linearly for low values of N_n ; in this regime almost all of the potential nuclei give rise to pores. At higher values of N_n there is little increase in the final N_p due to increased N_n . In this regime the number of pores which nucleate early is sufficient to ensure that the balance between hydrogen entering the pores and hydrogen rejected at the solid-liquid interface is reached at a value of s which is low enough so that nucleation of pores from sites with higher thresholds is prevented.

Figure 6-10 combines the effects of changing C_H^i and s_{min} upon the relationship between N_n and N_p . A C_H^i of 0.6 (mol/m³) results in greater R_a and R_m than with a C_H^i of 0.4 (Figure 6-10(a) and (b)); and lowering the s_{min} (filled symbols) from a ratio of 2.2 to 1.7 increases the

size slightly; this effect is more significant for the lower C_H^i level. The lower s_{min} causes a greater number of pores N_p (Figure 6-10(c)) especially at high values of N_n where the effect of decreasing s_{min} is greater than the effect of increasing C_H^i . The combined effects (Figure 6-10(d)) result in a net increase in percent porosity for increased C_H^i or decreased s_{min} , with the effect of s_{min} being more pronounced for low values of C_H^i and high values of N_n .

The results are quite sensitive to N_n and s_{min} but in a non-linear fashion, exhibiting a transition in behaviour as described above. These parameters N_n and s_{min} , are intended to represent the number and the distribution of effectiveness of the nuclei present, and these results reflect the sensitivity of the final porosity to the nucleation process in castings. The best correspondence was found by setting N_n at 4 mm^{-3} and s_{min} at a supersaturation ratio of 1.7. This low value of supersaturation indicates a mechanism such as Type III or IV according to the classification of Jones *et al.* [34] described in Chapter 2.

From the comparisons between the model and the experimental work, it appears that the range of nucleation parameters in which the sensitivity is great is just that range which is accessed by the experiments.

However, one important limitation of the model may have reduced the predicted pore size, the assumption of cell-centred spherical pores. Once the pores grow larger than one cell, the growth of the pore is artificially restricted by the requirement that hydrogen enter the cell in which the pore is centred before it can enter the pore. This may help explain the reduced pore size in the model compared to the XTGS results, but still does not explain why the pores are larger than those shown by Fang *et al.* [56]. However, the use of larger cells would reduce the resolution available for the initial nucleation distribution and final pore number density. In the next chapter, the results of extending the model to allow each pore to occupy multiple cells are presented.

If the pores nucleate when the fraction solid is quite large, then impingement with the solid should affect the pore size. Assuming that the liquid wets the solid, the pore surface would be restricted to a curvature radius limited by the distance between solid particles, (dendrite arms or grains) thus increasing the pressure. The concentration at which the pore will be at equilibrium with the solution will then be increased according to Equations 3-17, 3-21, and 3-22, resulting in less gas at higher pressure in the pores for a smaller P overall. This may explain why the pore size and percentage is over predicted compared to the results of Fang *et*

al. in Figure 6-7. In the next chapter, the results of modifying the pore growth to approximate this interaction are presented.

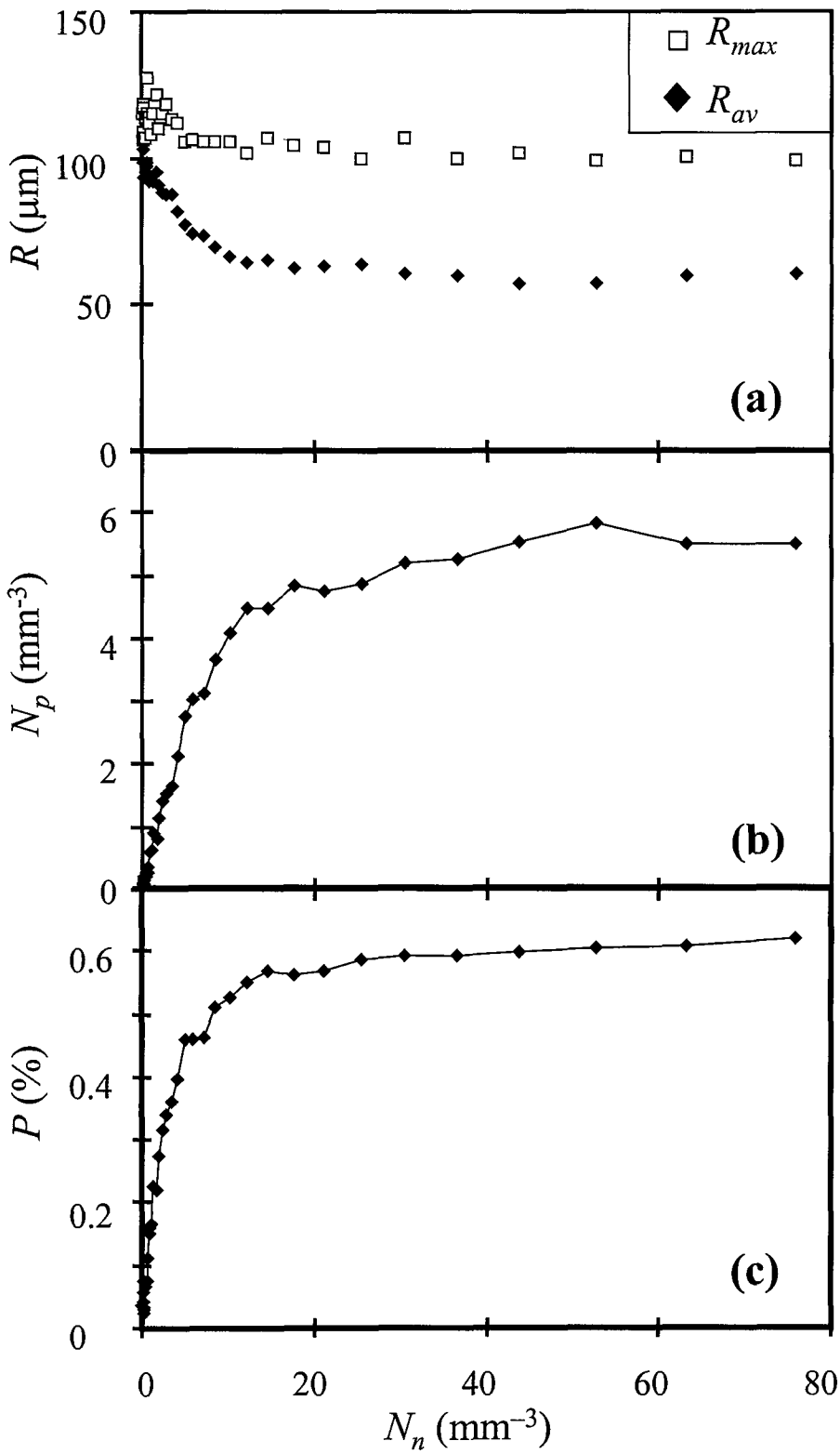


Figure 6-9. The effect of varying the number density of input nuclei, on (a) the average and maximum pore radius, (b) the number density of pores, and (c) the percentage porosity.

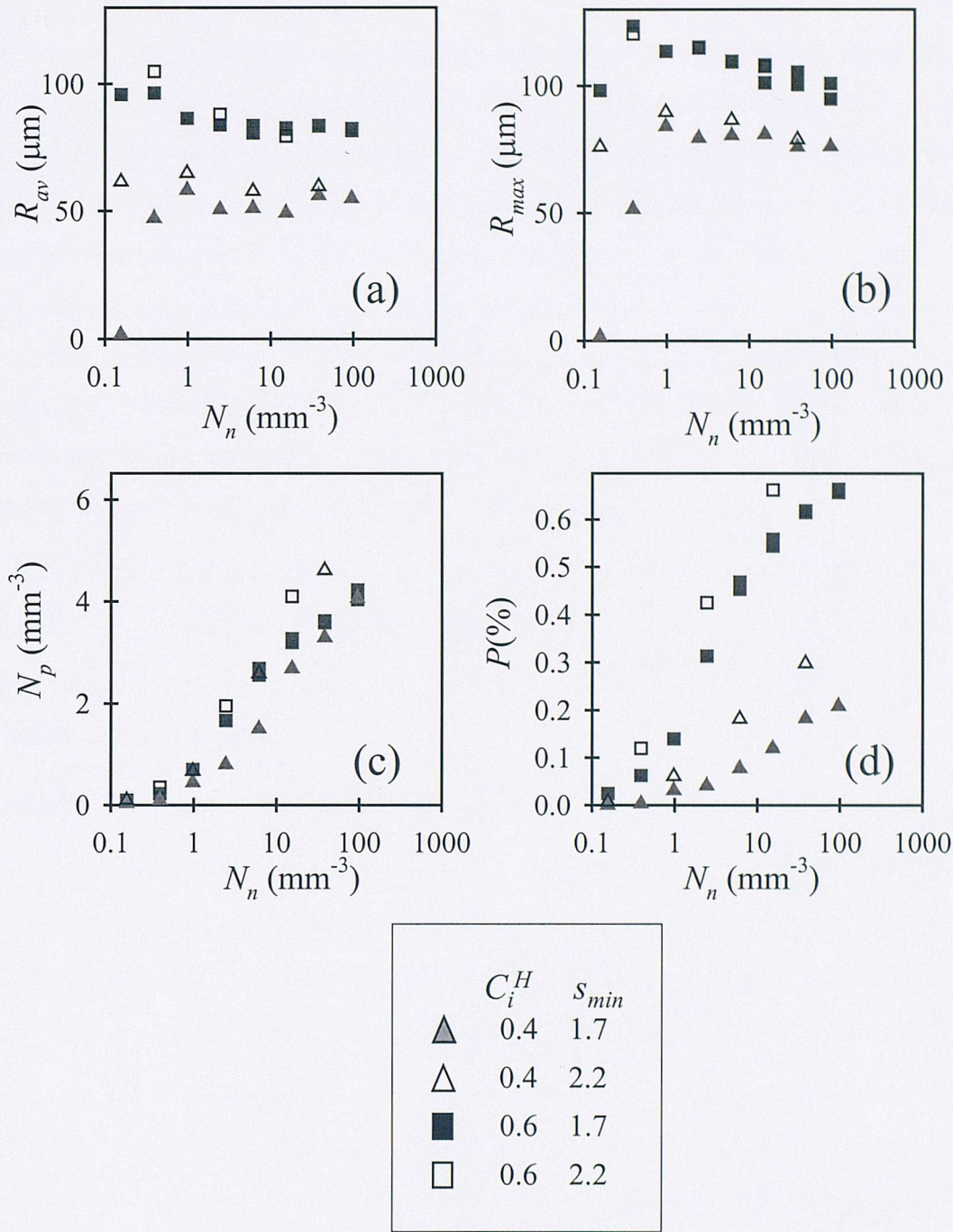


Figure 6-10. The effect of changing s_{min} , and the effect of changing C_i^H upon this relationship. For clarity, the average and maximum pore radius responses are separately graphed. (a) The average radius, (b) the maximum radius (c) the number density and (d) the percentage porosity.

6.3. Wedge Casting in A-356 Alloy

In this section, the porosity model including the complex shape was used in order to help predict the maximum expected length of pores in an experimental wedge casting. The casting was simulated by applying a macroscopic heat-transfer model to the casting geometry to calculate the thermal history at each position. The CA technique was used to predict the pore responses, including maximum length, for representative volumes. The CA technique uses a large amount of computer memory to perform the calculations. At this time, the most efficient way to make use of the results of this model to design industrial castings is to use constitutive equations derived by applying the model over a selection of values of the critical process variables, and then statistically reducing the data via multiple regression. This produces equations that may be applied at a low computational cost.

The CA model was applied to 100 different parameter values representing 10 levels of t_s and 10 levels of C_H^i . In addition, 20 of these were repeated in order to help gauge the effect of random variables on the porosity measurements, thus improving the estimate of the significance of the statistical fit.

The porosity data were regressed against t_s and C_H^i . Relationships of the power law form including C_H^i in the exponent were found to have very good significance ($p < 0.01$) for predicting the R_a and L_{max} whereas the percentage porosity was better predicted by including a linear relationship with C_H^i and an interaction term with $\ln(t_s)$, in which the linear relationship with the initial hydrogen content dominates. See Appendix B for the regression statistics.

However, the effect of shrinkage upon the pores in the wedge casting could not be discounted. The effect of the pressure in the model may only at present be simulated by changing the applied pressure, and this has the effect on the porosity responses shown in Figure 6-11, the results of changing the pressure between 0.25 and 2.25 bar. Reduced pressure increases the size and number of pores whereas increased pressure has the opposite effect. Above about 1.8 bar, the model results show no pores or only a single pore in the model domain. The resulting number density is therefore not accurate at this end of the range without using larger domains at the cost of increased computation time on the order of the third power of the linear dimension.

Preliminary trials indicated that a reduction in the applied pressure in the model would improve the correspondence between the model and the experiment, so a reduced pressure of

0.6 bar was used in this exercise. However, this was still not sufficient because of the difference in shrinkage behaviour at different parts of the wedge. Thus, those areas with longer solidification times experienced greater reductions in pressure due to shrinkage; this effect could not be included in the current model as the pressure is uniform and the flow of fluid is not included. Experimentally, this effect could be reduced by improving the insulation above the wedge, thus preventing a solid skin from forming at the top and allowing the top riser section of the wedge to act as a more effective feeder.

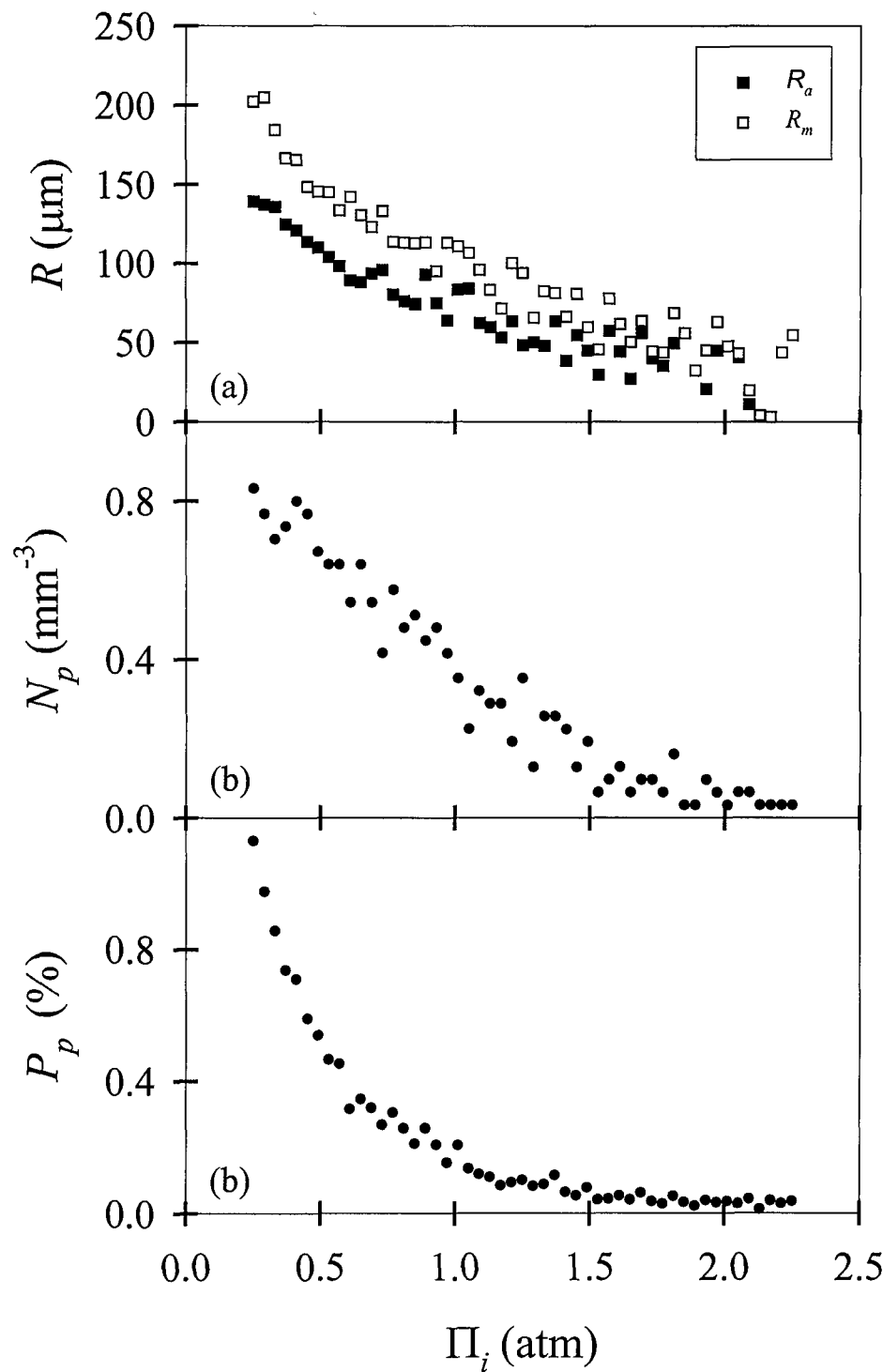


Figure 6-11. The effect of applied pressure on (a) the average and maximum pore radius (b) the pore number density and (c) the percentage porosity.

6.3.1. Constitutive Equations from the CA Model

These relationships were used to predict the porosity responses in the CA micromodel, and the mechanical properties were then predicted using the empirical results from the wedge casting. Figures 6-12-6-14 illustrate the response surfaces for L_{max} , d_{avg} and P_p . The equations derived were:

$$R_{avg} = 18.91t_s^{0.91 \times C_H^i} (\mu m). \quad (6-2)$$

$$L_{max} = 51.42t_s^{1.57 \times C_H^i} (\mu m). \text{ and} \quad (6-3)$$

$$P = -0.372 + 0.184C_i \ln t_s + 4.04C_H^i (\%). \quad (6-4)$$

where P is taken as zero if equation 6-4 predicts a negative value. The analysis of variance (ANOVA) tables for the above regressions are summarised in Appendix B.

Figure 6-12 illustrates that increasing either the local solidification time or the hydrogen content will increase the maximum pore length (L_{max}). This is the same trend was found experimentally by Tynelius *et al.* [29] and Fang and Granger [50]. They concluded that the initial hydrogen content had the largest effect on the percentage porosity, whilst increasing the local solidification time was the second largest influence.

Figure 6-13 gives the average pore radius R_a as a function of local solidification time and hydrogen content. Increasing either C_H^i or t_s increases R_a to a similar extent as the maximum pore length. This also correlates well to the findings of Tynelius *et al.* [29] and Fang and Granger [50].

Figure 6-14 illustrates that the percentage porosity is most dependent upon the initial hydrogen content, and less dependent upon the local solidification time, agreeing with Tynelius *et al.*'s finding that C_H^i is the most important factor in P [29].

These equations were applied to a macromodel of a wedge-shaped test casting run using the commercial heat-flow simulation package CAP[§] to calculate the thermal history.

A two-dimensional CA model, including the complex pore algorithm, was run for a slice of the wedge, using a constant temperature gradient approximation to the CAP model results.

[§] CAP by EKK Inc. 2065 West Maple, Walled Lake, MI 48390.

Figure 6-15 illustrates the results of (a) an experimental wedge casting, polished along a vertical section, with a larger magnification micrograph inset, (b) the CA model for the vertical slice of half the wedge, with a larger scale image inset to compare with (a) and (c) the CAP plus CA-derived prediction for L_{max} (Equation 6-3). The correspondence of the pore appearance between the model and the experiment is quite good.

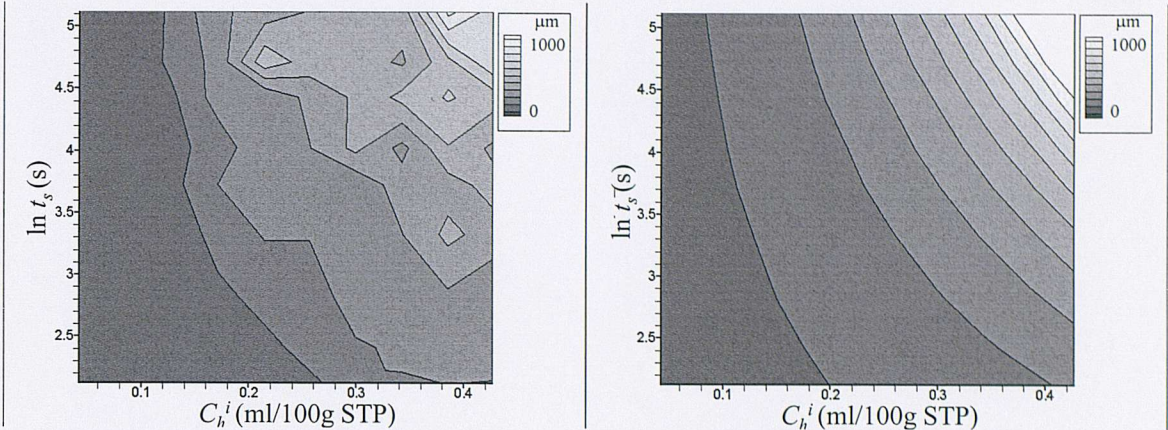


Figure 6-12. Contour plots of L_{max} : (a) CA model predictions for 100 different values of solidification time and initial hydrogen content; and (b) fitted response surface derived from the results of (a) including repeats.

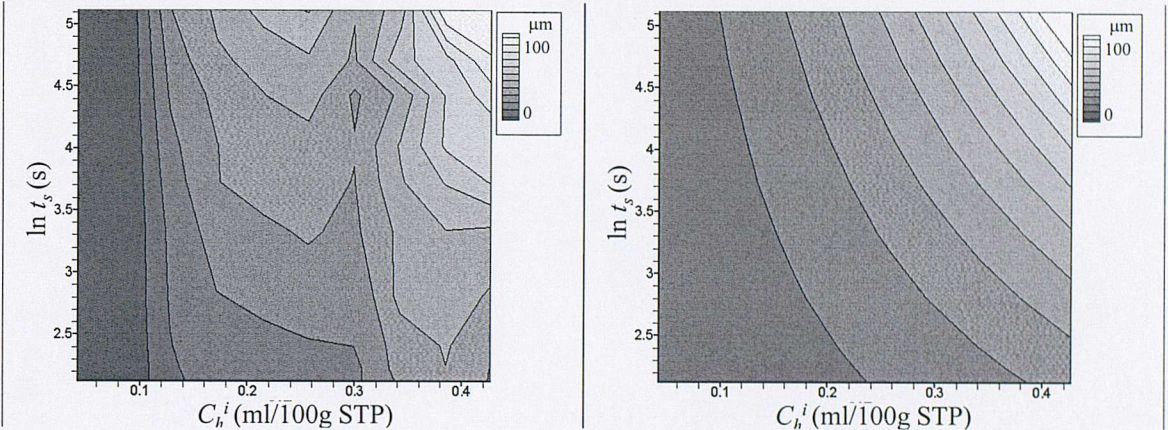


Figure 6-13. Contour plots of R_a : (a) CA model predictions for 100 different values of solidification time and initial hydrogen content; and (b) fitted response surface derived from the results of (a) including repeats.

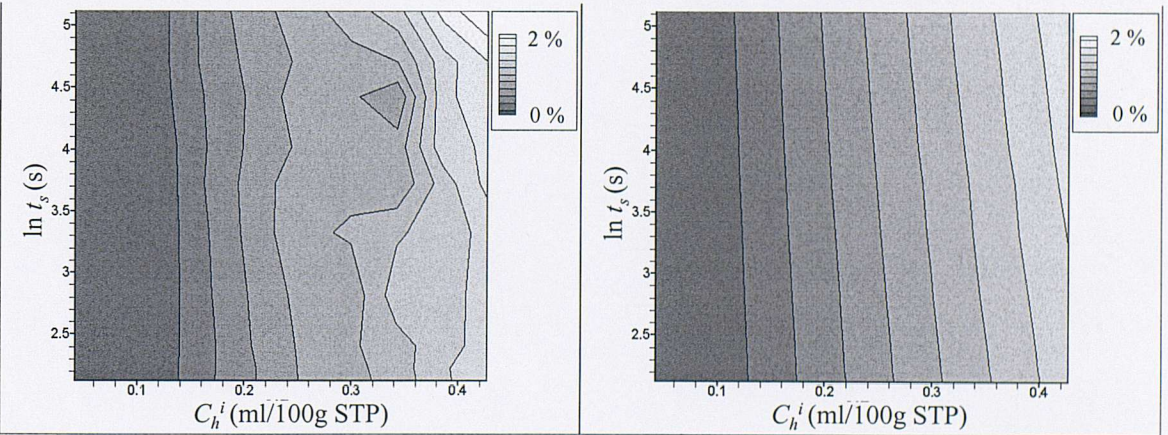


Figure 6-14. Contour plots of the P : (a) CA model predictions for 100 different values of solidification time and initial hydrogen content; and (b) fitted response surface derived from the results of (a) including repeats.

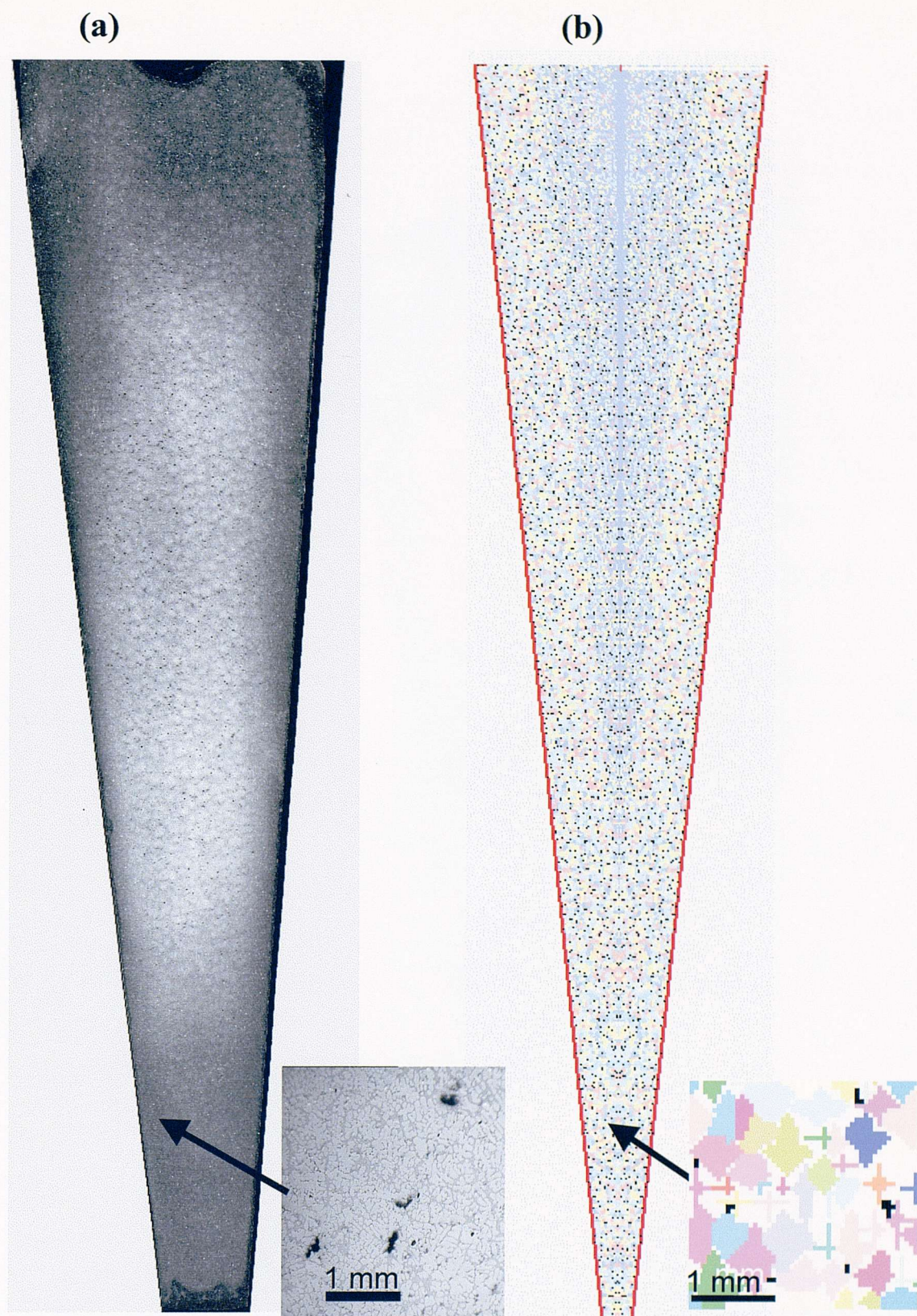


Figure 6-15. Results for a wedge casting. (a) Macrograph of a polished, unetched slice with a micrograph (inset) showing the appearance of the porosity. (b) Results of a CA model of a slice of a wedge, with a larger scale section(inset) also showing the appearance of the porosity (black areas) (Polished wedge specimen courtesy J. Yi).

(c)

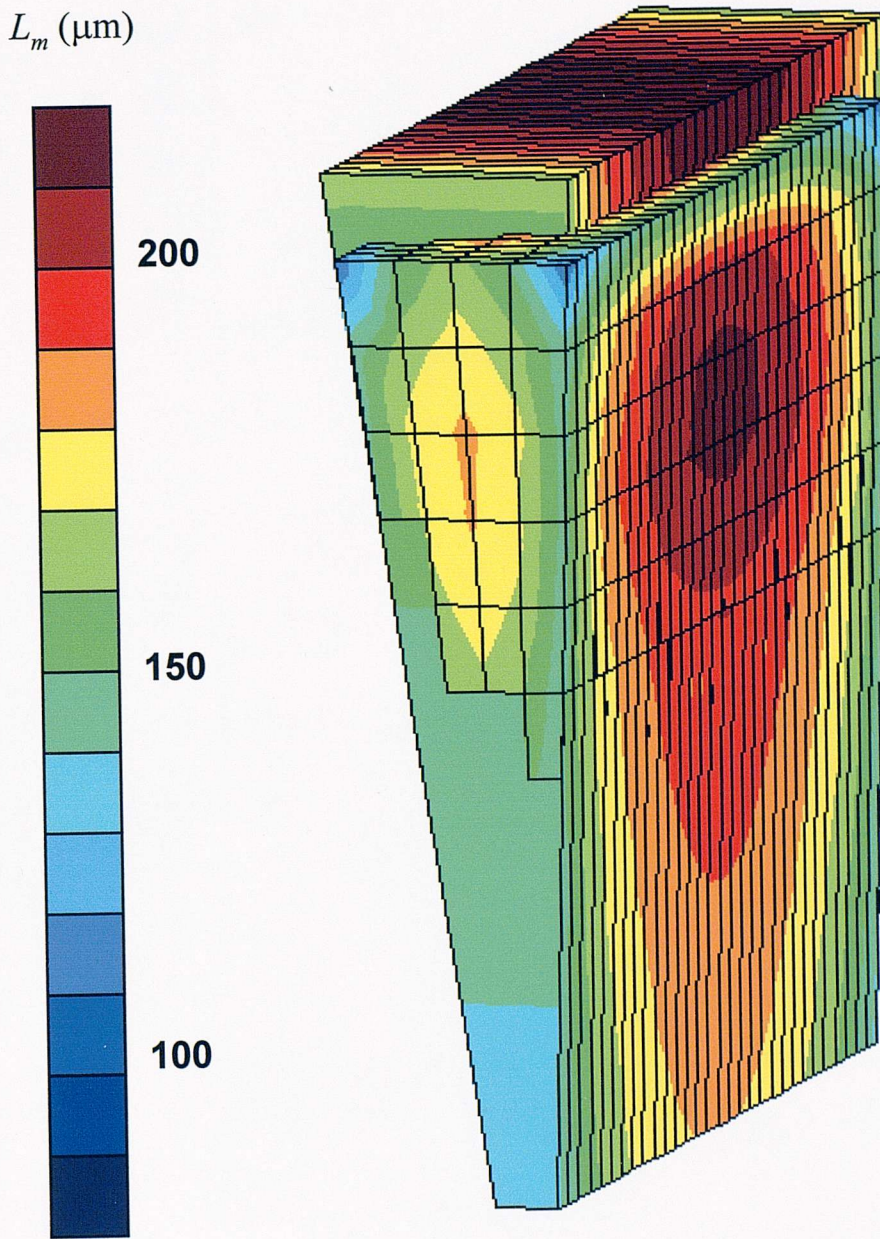


Figure 6-15. Results for a wedge casting. (c) Results for the maximum pore dimension L_m calculated by applying the regression equation derived from the CA results to a macroscopic model of heat flow in the wedge. (Macromodel courtesy Y. Youssef and A.C.Yeh)

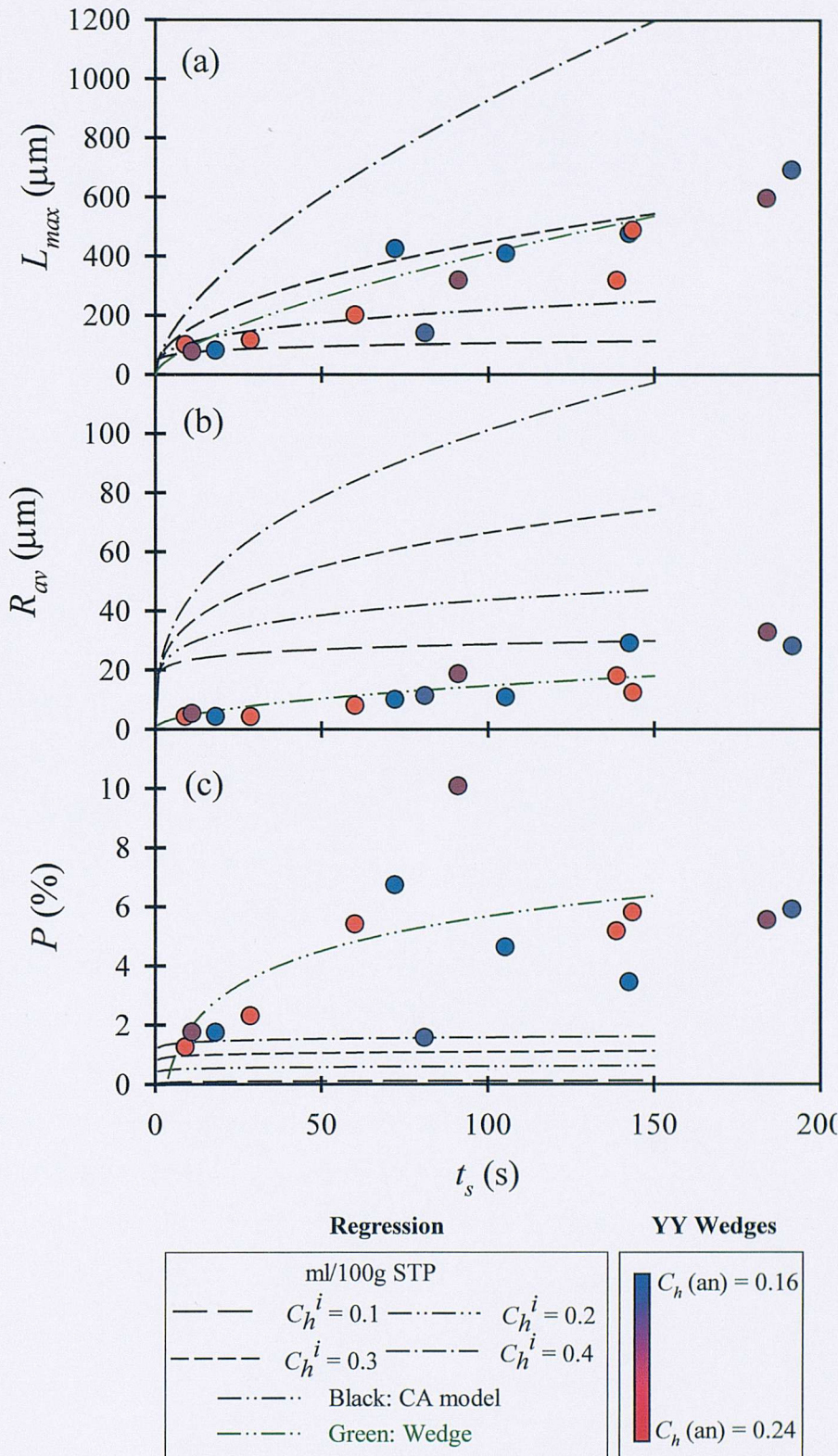


Figure 6-16. Comparison between the porosity responses predicted by the regression equations based upon: the CA results (black lines), and the observed responses from test wedge castings (Y. Youssef [109], green lines) (a) Maximum pore length L_{max} , (b) Average pore radius R_a , and (c) Percentage porosity P . The original data from the test wedges is shown coloured according to the analysed hydrogen content $C_h(\text{an})$.

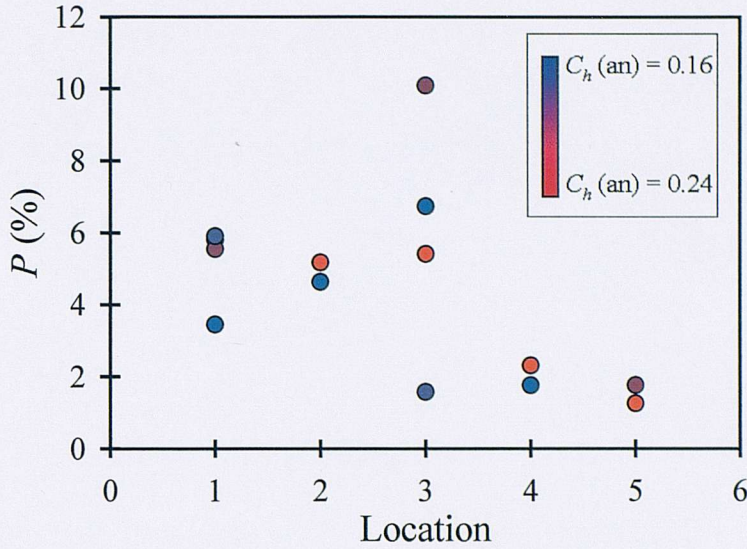


Figure 6-17. The P results from the wedge experiments, grouped by location (1=top, 5=bottom) of the wedge, showing a stronger correlation than that for solidification time, Figure 6-16.

A sufficient range of C_H^i was not achieved in the wedge to reliably quantify its effect upon the porosity, so the value at 0.2 ml/100g STP is shown on Figure 6-16 to compare with the results of the CA regression. The predicted L_{max} shows the best correspondence with the L_{max} as observed from the wedge, Figure 6-16 (a). The predicted L_{max} and P are greater than the experimental values; this is most likely due to the effect of shrinkage in the experiment which, as discussed in Chapter 3, has not been incorporated into the CA model. The original wedge P values show a large amount of scatter in the results (coloured symbols) and lack correlation with the solidification time or the hydrogen content, whereas it is much better correlated with the approximate location from bottom (narrow end) to top (wide end) of the wedge, Figure 6-17. This indicates that the macroscopic feeding as a function of position is more important than the microstructural development for the total volume of porosity. The CA model results for P are virtually independent of t_s except where t_s is very low, indicating that all the available hydrogen is incorporated into the pores, any further increase in volume must be due to decreased pressure, solubility different from that assumed, or externally connected macroporosity (especially at location 1).

The average equivalent spherical radius, R_{av} , shown in Figure 6-16 (b), is greater in the model than the metallurgically measured equivalent circular radius of pores from the wedge, and this combined with the above observations indicates that many of the observed pores are cross-sections of elongated pores and do not give a good indication of the actual volume of the pore.

Thus, the L_{max} response appears to be the more robust and hence useful parameter, in that it corresponds with the observed results especially at the low end (low t_s) of the wedge. The maximum dimension is most useful for predicting the fatigue properties of the casting and thus should be the subject of further modelling effort.

7. APPLICATION: AL-MG

In this chapter, the model is used to predict the porosity formation during the direct chill (DC) casting of aluminium-magnesium alloy. Experimental and macromodel results were provided by NLM** for instrumented DC castings, which were sectioned and examined metallographically, for validation of the model. For this alloy system, the porosity model including complex shaped pores and the restricted bubble growth assumption is used. The industrial problem which NLM was investigating was the production of a product suitable for high-vacuum applications, so even a relatively small pore could contain sufficient gas to act as a 'virtual leak' if it connects with the final surface of a product.

The results of the examination of three DC ingots were used to validate the porosity model.

7.1. Experiments

Laboratory scale DC cast slabs of aluminium with 2, 4 and 6wt% Mg were produced by NLM Nikkei Research & Development Centre with a cross-sectional dimension of 250 mm by 400 mm. The metal was added at a temperature of 1003 K and cast at a rate of 0.97 mm/s. Grain refiner was not used and the cooling water supply was 2.8 litres/s.

The Al-4Mg cast was instrumented with K-type thermocouples attached to stainless steel rods placed at a distance from the rolling surface of the slab of: 5, 20, 40, 60 and 80 mm. The thermocouples were inserted through the starting block and set at 200 mm above the starting level. The thermocouple locations were confirmed by radiographic analysis after casting to ensure they had not moved.

Metallographic samples were cut from the surface to the centre of the slab for polishing and examination. Using optical microscopy, the percentage porosity and pore size were measured using a commercial image analysis package. Only the pores whose equivalent diameters were more than 6 μ m were measured and included in the values of average pore size.

Macroscopic scale fluid flow and heat transfer models of these castings were run at NLM using CAPFLOW^{††} in order to predict the temperature profile which could then be used to determine the conditions for the CA model. These three casts allowed a range of thermal conditions and alloy compositions (both Mg and H₂ levels) to be varied to investigate their effect upon porosity. The conditions that were used are listed in Table XIV along with the

** This work resulted from a collaboration with Dr. Hiromi Nagaumi of Nippon Light Metals (NLM) company.

†† Provided by EKK Inc, 2065 West Maple, Walled Lake, MI 48390.

results of the macroscopic model. Measured and predicted cooling curves for the 4%Mg ingot are shown in Figure 7-1. The cooling was approximated as a constant cooling rate for each location in the billet, determined by interpolating the experimental results, as shown in Figure 7-2. Three magnesium levels were used: 2, 4 and 6wt%. Within each casting, significant variations in the cooling rate/local solidification time occurred from the rolling surface to the centre.

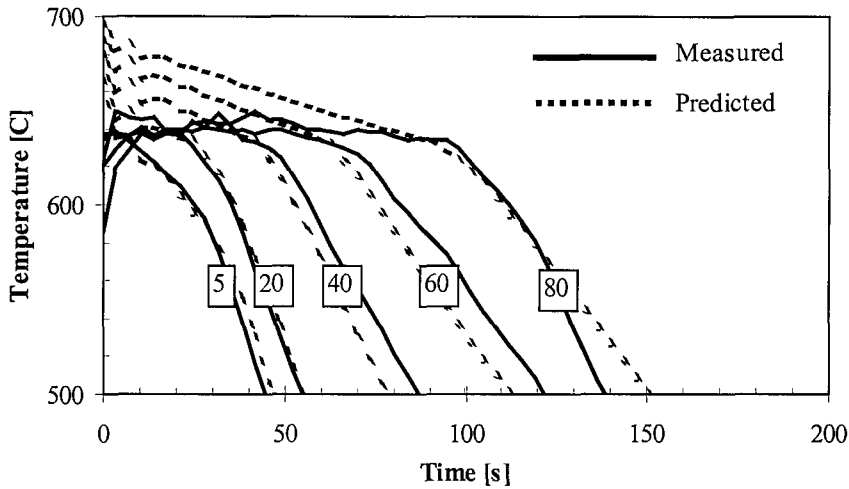


Figure 7-1. Measured and predicted cooling curves for five locations from the billet surface: 5, 20, 40, 60 and 80mm.

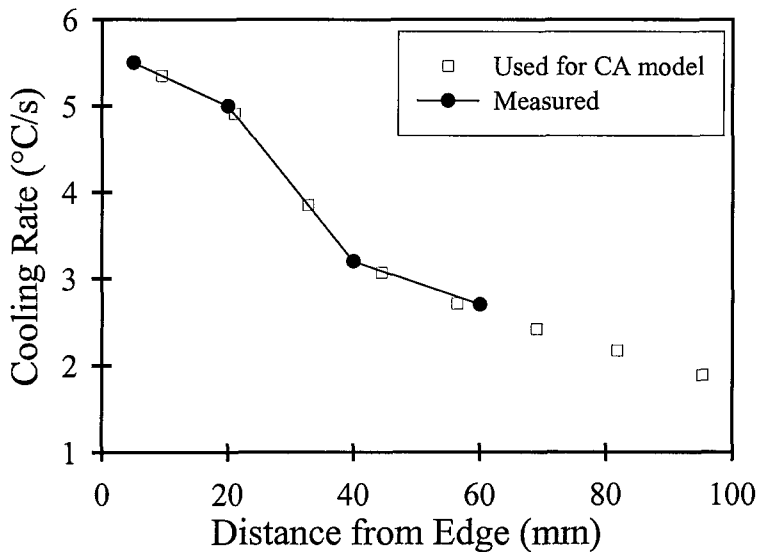


Figure 7-2. The constant cooling rate used in the model as a function of distance from the billet surface, interpolated from the measured results.

Table XIV. Measured and CAPFLOW predicted local solidification times and cooling rate (averaged over approximately 560-600°C) for the Al-4wt%Mg DC cast ingot.

Location mm	Local Solidification Time		Cooling Rate	
	Measured s	Predicted s	Measured °C/s	Predicted °C/s
5	26	25	5.5	4.7
20	29	25	5.0	4.8
40	30	27.5	3.2	3.9
60	44	30	2.7	2.8
80	63	42.5	2.3	2.4

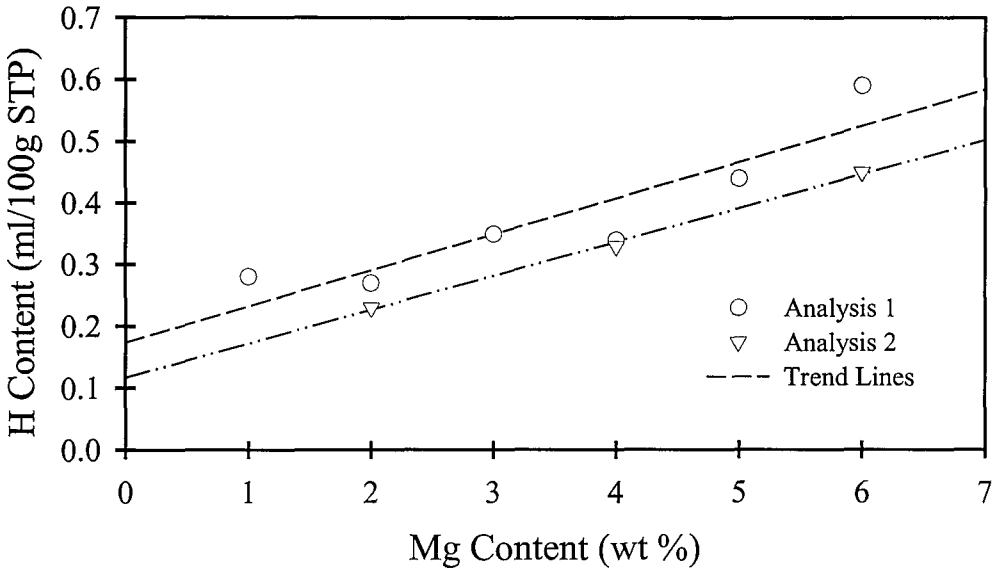


Figure 7-3. Hydrogen content versus wt% Mg. Two separate analyses of the samples are shown with fitted lines to indicate the trends. Analysis 1 – Ransley specimens analysed at the NLM laboratory; Analysis 2 – Leco subfusion analysis of specimens cut from the billet analysed by Sci Lab Analytical Ltd.

In the experiments, it was not feasible to uncouple the Mg and H₂ levels. The experimentally determined hydrogen content under the normal processing conditions (by producing test specimens during the production run) is shown in Figure 7-3 -- Analysis 1, and the hydrogen content determined after casting (from test pieces cut from the billets) is shown as Analysis 2, along with fitted lines indicating the trends. Increasing the magnesium level has a dramatic effect on the hydrogen absorption at the surface prior to casting with the 6wt.% magnesium alloy containing more than twice the hydrogen measured in the 2wt% alloy. The high hydrogen levels occurred despite the use of an in-line rotary degasser. As described in

Section 2.3, both the solubility and the rate of pickup of hydrogen are increased by the presence of Mg in the alloy.

The model is first validated against the experimental results, and then the effect of altering key process parameters upon the model predictions are investigated in order to determine how the process might be altered to minimize the porosity. The conditions used for all of the model runs are given in Table XV, unless otherwise stated.

7.2. Model Validation

The results of the direct comparison for percentage porosity are shown in Figure 7-4. The conditions used are those listed in Table XV, except the initial magnesium (2, 4 and 6wt%) and hydrogen levels (see Figure 7-3) were varied to match those in the three experimental DC cast ingots, together with the appropriate cooling rates interpolated from the values in Table XIV to the location at which the percentage porosity was measured (shown in Figure 7-2). Note that only the 4wt%Mg casting was instrumented with thermocouples, therefore the values from this casting were used for the 2 and 6wt%Mg casts, introducing a possible source of error.

The nucleation parameters were chosen empirically. Preliminary models were run to determine suitable values. The resulting choices, $s_{min} = 3.5$ and $N_n = 4 \times 10^{11} \text{ m}^{-3}$, differ from the choices used for the Al-Si models in the previous chapter; the number of nuclei is greater but the supersaturation required for the first nucleation is also greater. This is likely due to the procedures used at the foundry to clean the melt so as to reduce the porosity to the observed level, combined with differences in the mechanism of nucleant particle formation. More effective cleaning would remove the most active nucleants, leaving smaller and less active heteronuclei which are, however, greater in number. If the surface oxide of the Mg containing alloys is less cohesive than that of the Si containing alloys, as suggested by the possible explanations for the increased H absorption by these alloys, then particles of oxide formed during melting and casting would be smaller and less likely to form folded layers entrapping pockets of gas.

The modelling parameters were chosen to allow suitable resolution for the grain and pore structures observed experimentally, while considering the stability and accuracy criteria discussed in Section 4.1.6. A cell size of 50 μm was chosen to allow resolution of the relatively finer microstructure compared with that of the XTGS experiments in Al-7%Si described in the previous chapter.

The hydrogen content as determined by the analysis of samples from the billets (Analysis 2, Figure 7-3) was used; if the higher values due to the Analysis 1 were used then nucleation of the pores in the 6 wt% Mg alloy simulation occurred before the onset of solidification. If this actually occurred in the experiments, the bubbles of hydrogen would tend to rise to the surface and the hydrogen would not be present during solidification. This could explain the difference between the two analyses in Figure 7-3.

Table XV. Default values used in the model of porosity formation.

Property	Symbol	Value	Units
Applied cooling rate	Δt	1.5	°C/s
Cube dimension	x	2.5	mm
Initial Temperature	T_0	640	°C
Grid Spacing	Δx	50	μm
Time Step	Δt	0.625	ms
Minimum Hydrogen Supersaturation Ratio at Nucleation	s_{min}	3.5	-
Potential Pore Nucleus Density	N_n	400	mm^{-3}
Hydrogen Solubility	S_H	as given in Eqn. 2-26	ml/100g STP
Effective Hydrogen Diffusivity	D_e	as given in Eqn. 2-29	mm^2/s
Hydrogen Partition Coefficient	k	0.1	-
Initial Mg Concentration		2, 4 or 6	wt%
Initial Hydrogen Content	C_H^i	0.23, 0.33, 0.45*	ml/100g STP
Al-H ₂ interfacial energy	γ	0.856	Pa m
Ambient Pressure	P_{atm}	101325	Pa

*The three hydrogen levels correspond to the three magnesium levels as related in Fig. 7-3.

Experimentally, the percentage porosity was observed to increase with both increasing distance from the rolling surface (increasing local solidification time) and with increasing Mg level. The model correctly predicted both these trends, providing an excellent prediction of the amount of porosity formed for the cases studied.

As will be discussed later in the model sensitivity section, the large increase in percentage porosity with increasing Mg is primarily due to the concomitant increase in H₂.

Experimentally, it was also observed that the effect of increasing the Mg/H₂ level on the number density and morphology of the pores was different at short solidification times from long ones (as summarized in the experimental results section above and shown in Figure 7-5).

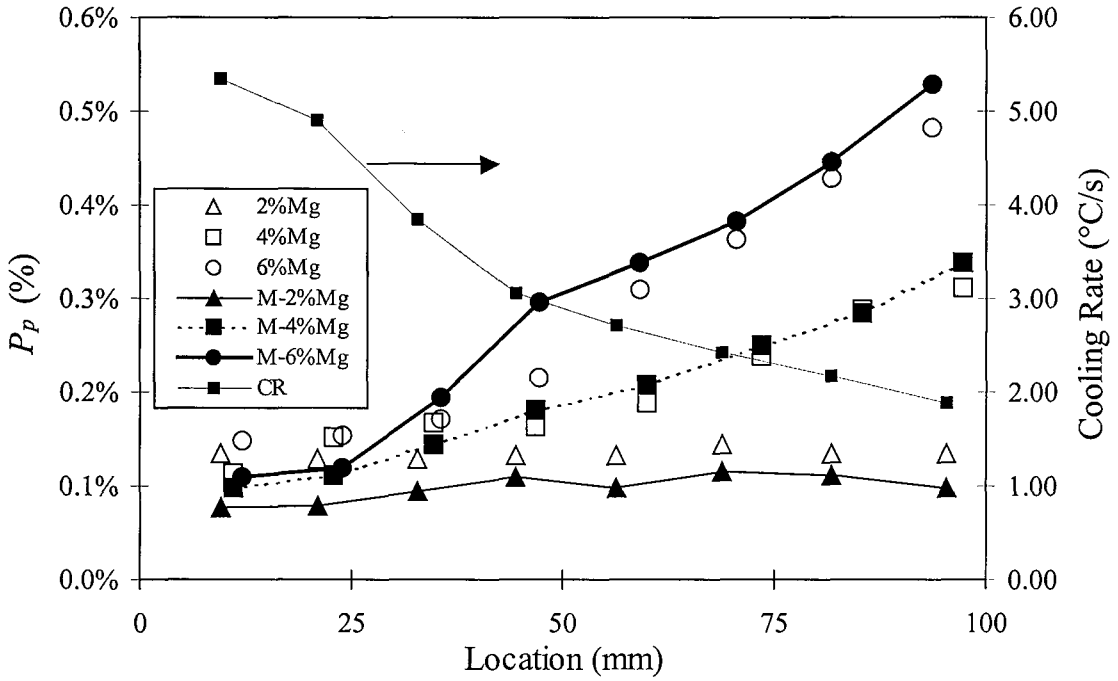


Figure 7-4. Predicted (lines) and experimentally measured (symbols) percentage porosity plotted at different distances from the billet surface for three Mg levels, 2, 4, and 6 wt%.

The model predicts this experimentally observed change in number density and pore morphology, as shown by the three-dimensional renderings of the final pore shapes in Figure 7-6. The four extreme conditions of a) 2wt%Mg and a short t_s , b) 2wt%Mg and a long t_s , c) 6wt%Mg and a short t_s , and d) 6wt%Mg and a long t_s , are shown to match the condition of the micrographs shown in Figure 7-5(i-2), 7-5(iii-2), 7-5(i-6) and 7-5(iii-6), respectively. Figure 7-6 illustrates that with increasing local solidification time (or distance from the chill face), fewer, larger pores are formed. The size increases sharply at the locations where the cooling rate decreases sharply, and increases less sharply where the cooling rate decreases less sharply. Near the billet surface, increasing the Mg (and H_2) concentration only has a minor effect on pore size, however the number density dramatically increases. Near the centre of the billet, the pore size increases and the pore morphology becomes much more tortuous as the Mg (and H_2) level increases. The amount of interaction between the growing pore and the developing microstructure was found to be a critical factor in correctly simulating this behaviour, with the restricting radius (as given by Equations 3-24 and 3-25) generating pressures in the pores of many atmospheres due to the Gibbs-Thomson effect (Equation 3-18).

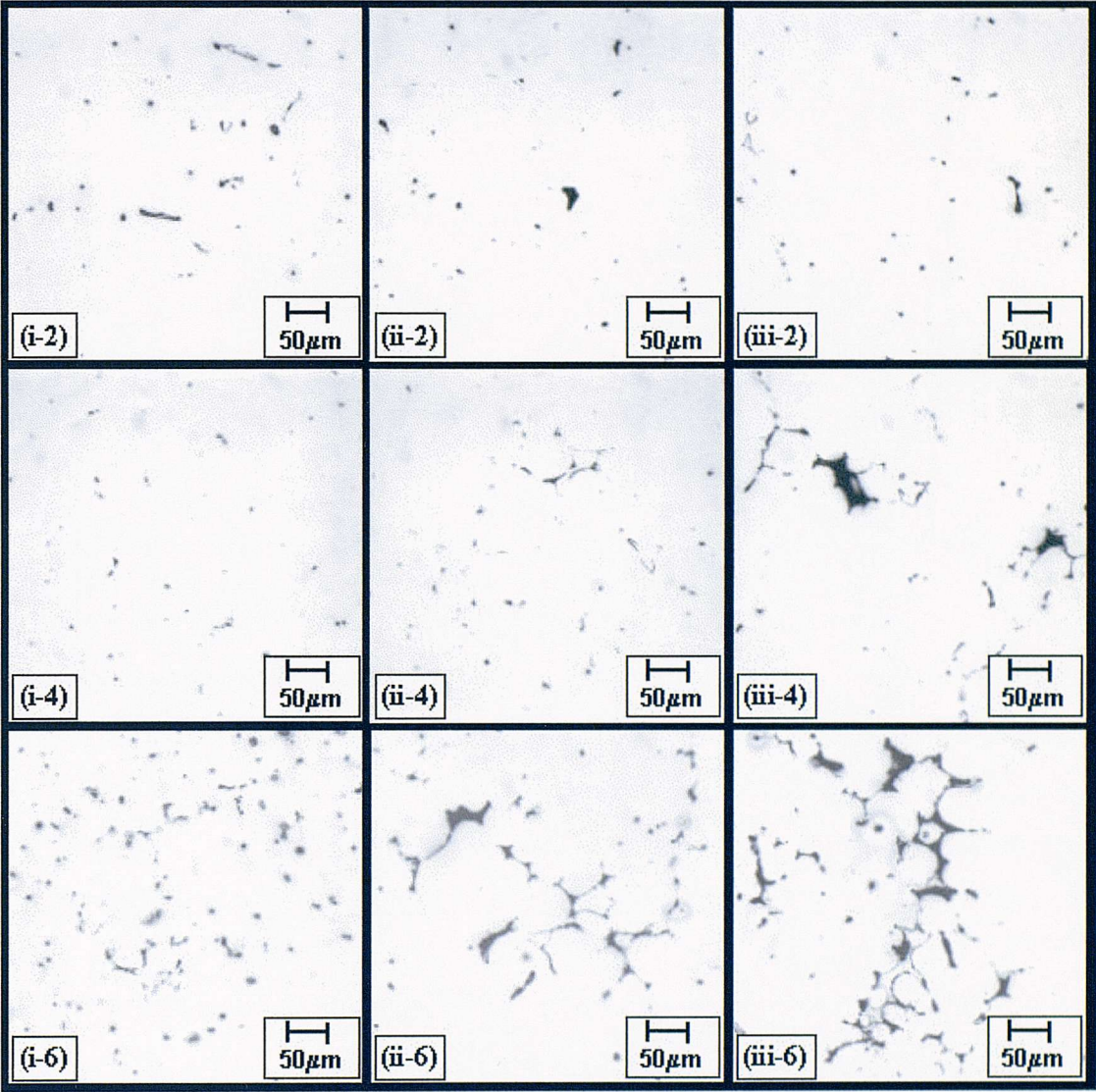


Figure 7-5. Typical light micrographs of the porosity at three locations for each of the three Mg levels cast. The location is designated by i) 10-20mm; ii) 60-70mm; iii) 100mm. The Mg level is designated by the 2, 4, 6, indicating the wt% magnesium. (Adapted from [118]).

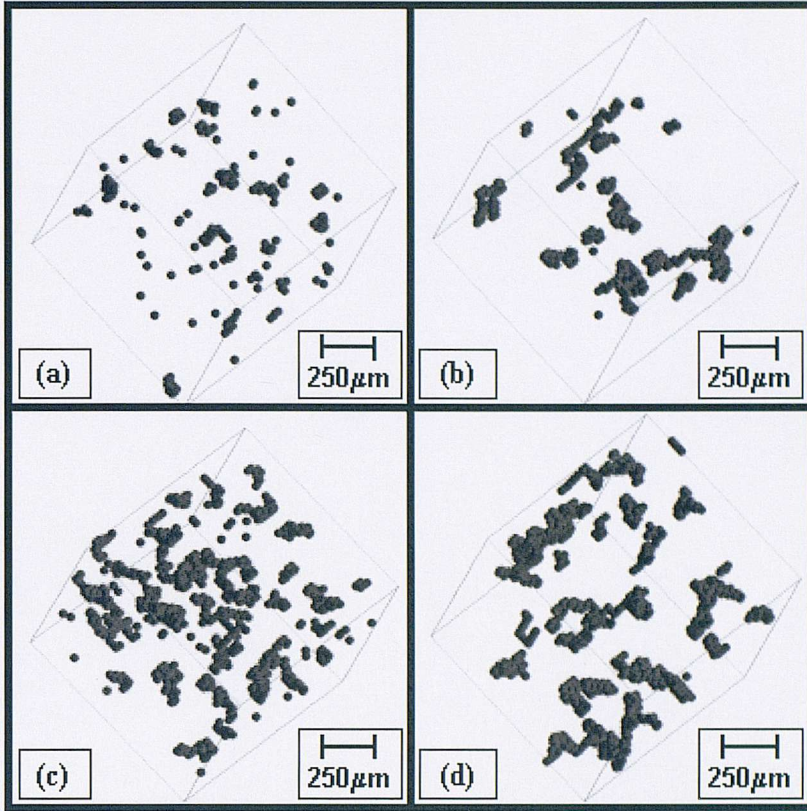


Figure 7-6. Simulated microstructures for the extreme cases 2wt%Mg with: a) $t_s = 20$ s, b) $t_s = 50$ s; and 6 wt%Mg with: c) $t_s = 20$ s, d) $t_s = 50$ s.

Together with the curvature restriction, the multi-cell model of pore growth allowed the long, tortuously shaped pores to be simulated (see Figure 7-6(d)) that were observed experimentally near the centre of the 6wt%Mg billet (see Figure 7-5(iii-6)). The under-prediction of the percentage porosity at low t_s (near the billet surface), was thought to be due to the failure of the empirically derived function for the restricting radius. The restricting radius could be studied by either performing experiments that allow the liquid region between the dendrites to be better characterized as a function of time (*e.g.* rapid quenched experiments) or by performing simulations at a scale that resolves the solid-liquid interface at a very fine level (*e.g.* using CAFD with a cell size of approximately $1\mu\text{m}$ or using a phase field technique).

In summary, the model predicts the observed experimental trends in not only the percentage porosity, but also in the morphological changes in the pores formed.

7.2.1. The restricting radius

The results which best fit the experiments were obtained by using an equation of the form of Equations 3-25 and 3-26 such that the parameters A_λ and b varied as functions of Mg concentration:

$$r_e = A_\lambda \left(\frac{dt}{dT} \right)^{(\alpha_1 + \alpha_2 Mg)} \tag{7-1}$$

where the parameter values are given in Table XVI.

Table XVI. Empirical parameters for the effective limiting radius.

Parameter	Value
A_λ	5.48E-05
α_1	1.003
α_2	-0.403

These parameters result in the variation of r_e with cooling rate as shown in Figure 7-7 The behaviour of the 2%Mg alloy is such that r_e appears to increase as a function of cooling rate rather than decrease as in the other alloys, indicating that the decrease in porosity for this alloy with high cooling rates is less than predicted even with a constant r_e . In other words, the pores are able to grow more at the higher cooling rates than is expected. One possible explanation is suggested by the results of the bubble surface simulation, Section 5.7.2. If the liquid is poorly wetting on the solid, a smaller spacing results in a lower pressure in the bubble. Therefore, a smaller actual spacing of the solid surfaces restricting the bubble would result in a larger effective spacing. This would require that the liquid become less able to wet the solid as the concentration of Mg decreases.

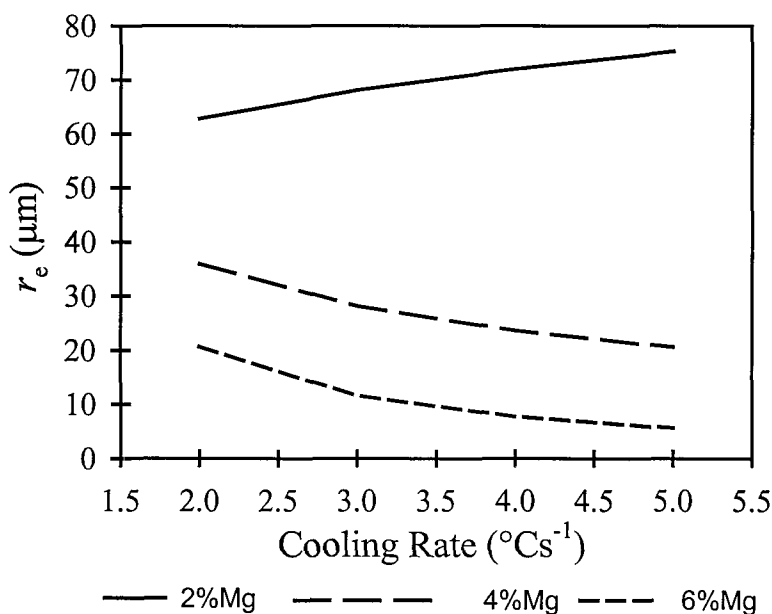


Figure 7-7. The empirically derived relationship between effective limiting radius for pore expansion r_e and the imposed cooling rate, for different AlMg alloys.

However, some other mechanisms could account for this behaviour by violating the assumptions upon which the model is based.

The effect of shrinkage, neglected in the model, should cause the reverse effect; those alloys with more Mg and hence longer freezing ranges should experience more pressure drop tending to expand the pores.

The grains may have a less dendritic structure, tending to be more spherical. If the grains do not form an interlocking dendritic structure, the pores may expand against the grains, moving them apart and hence the pressure would be less than the assumptions would predict. Gas bubbles may more easily detach and float out of the mushy zone and out of the melt, thus not forming porosity at all. This possibility is also suggested by the difference between the analysis of Ransley specimens cast from the production melt and the Leco analysis of specimens cut from the final billets, Figure 7-3.

The size and nature of intermetallic particles formed from the minor alloy components could be different, so particles with the poorly wetting characteristics may be present. A careful microscopic comparison at high magnification might help to indicate such a difference.

The effect of macrosegregation of H may be different, resulting in a profile of porosity versus ingot location which is not truly representative of the porosity which would be formed by cooling an entire sample at the observed or predicted cooling rate for that location. This could

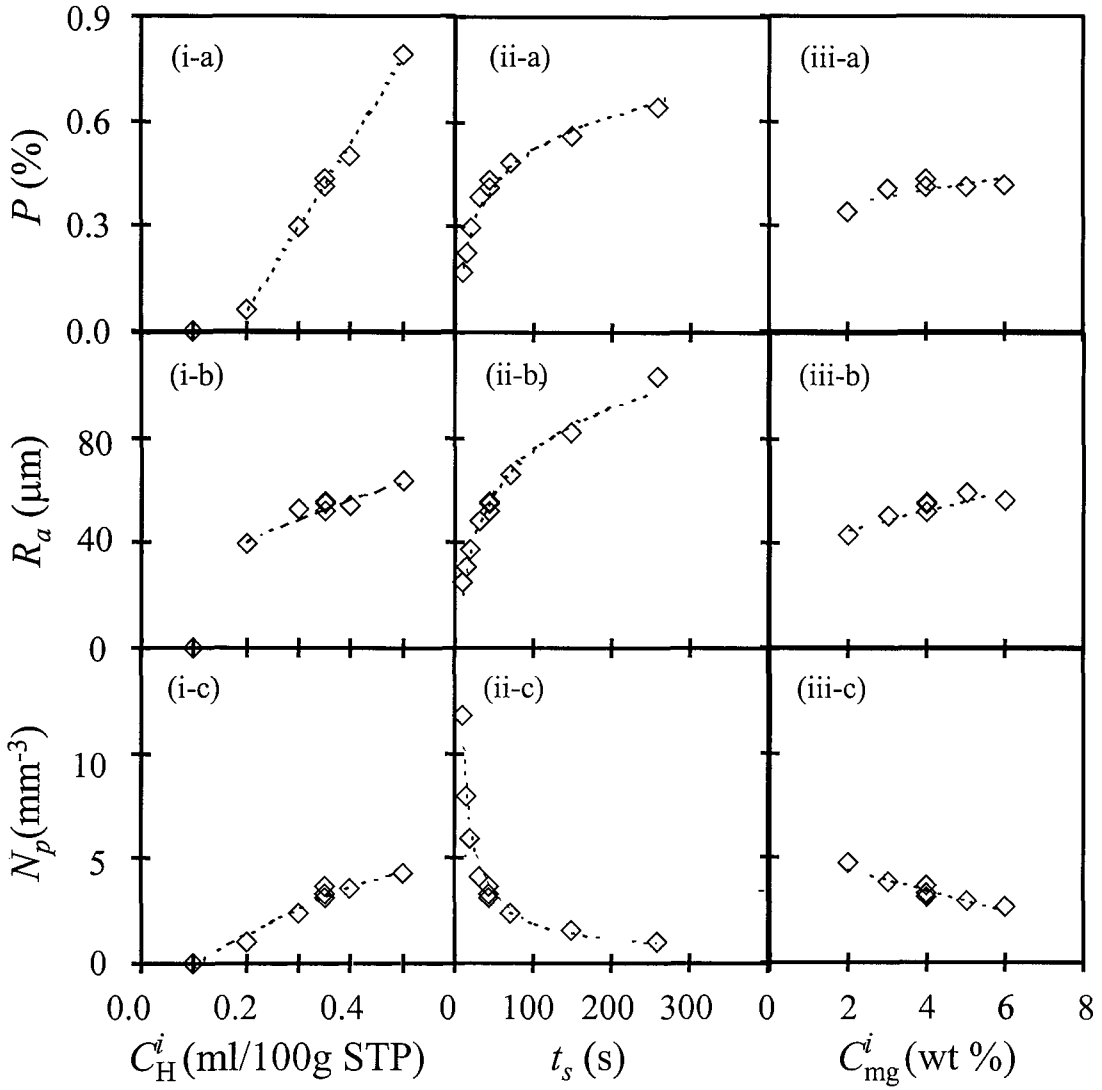


Figure 7-8. Sensitivity of the porosity model, showing the effect of varying i) initial hydrogen concentration, ii) local solidification time, and iii) initial magnesium concentration on a) percentage porosity, b) average equivalent radius, c) pore number density. Fitted lines are displayed to indicate the trends.

be tested by using the model in the fully coupled mode in which the macromodel for the heat flow and fluid flow exchanges information at each step with the micromodel for grain growth and porosity formation.

7.2.2. Effect of Process Parameters on the Predictions

In this section, the effect of altering key process parameters upon the model predictions are investigated, namely: i) initial hydrogen concentration, C_H^i ; ii) local solidification time, t_s ; and iii) initial magnesium concentration, C_{mg}^i . These results are summarized in Figure 7-8. For all of the sensitivity study runs, the conditions used are given in Table XV, unless otherwise stated.

Influence of Initial Hydrogen Concentration

Increasing the hydrogen content has the effect of increasing the percentage porosity, pore size and pore density (see Figures 7-8i-a, 7-8i-b and 7-8i-c, respectively). Increasing hydrogen content causes the percentage porosity to rise linearly, its effect on the pore density is more complicated. Initially, the pore density increases linearly with hydrogen content; however, this trend does not continue and the rate at which the pore density increases diminishes with time. Increasing the hydrogen content has the effect of increasing the driving force for nucleation and consequently, the rate at which new pores are formed. It also causes pores to form earlier in the solidification process. Once nucleated the pores can grow rapidly, acting as hydrogen sinks and lowering the hydrogen content of the surrounding liquid, thus reducing the driving force for further nucleation. As the pores grow and solidification progresses, the shape of the pores becomes constrained by the growth of the solid dendrites, such that they become fairly elongated in shape (Figure 7-9 shows a simulation of this effect). This has the effect of reducing the distance which the evolving hydrogen has to diffuse to reach the growing pores, as can be inferred from the iso-contours of hydrogen concentration shown in Figure 7-9.

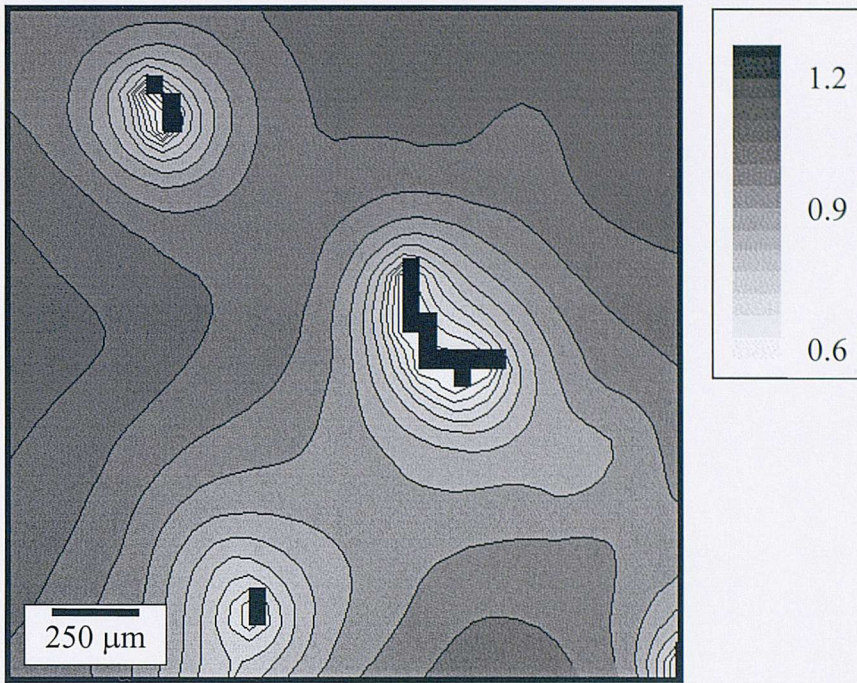


Figure 7-9. Example of how the multiple cell pore affects the local concentration of hydrogen. The pore is the black shape, the lines are contours of hydrogen iso-concentration (ml/100g STP).

Influence of Local Solidification Time

When the local solidification time is increased (*i.e.* the solidus and liquidus temperatures are fixed and the cooling rate between these two points decreased), both the size and percentage of pores increases whilst the pore density decreases (see Figures 7-8ii-a, 7-8ii-c and 7-8ii-c, respectively). This is simply due to the fact that as the solidification time decreases, the rate at which hydrogen is accumulated in the liquid is reduced, and the rate of pore nucleation is reduced. Once nucleated, the pores grow, depleting hydrogen from the surrounding liquid and reducing the driving force for further nucleation. As a result, increasing the local solidification time has the effect of producing fewer and larger pores.

Influence of Initial Magnesium Concentration

When studying the effect of magnesium concentration on porosity evolution for modelling purposes, the initial hydrogen concentration was maintained constant for all magnesium concentrations. Although increasing the magnesium content has a small positive effect on the hydrogen solid solubility, the major effect with respect to the model is the effect it has on the liquidus and solidus temperatures. Increasing the magnesium content decreases both the solidus and liquidus temperatures and has the effect of increasing the freezing range. Maintaining a constant cooling rate between the solidus and liquidus, the local solidification time increases with magnesium concentration and the same trends observed in the previous

section were observed here (as illustrated by comparing Figures 7-8iii-a to 7-8iii-c). In the experiments, the Mg level could not be varied independently of the H_2 level; therefore, experimentally this minor effect was subsumed by the much greater influence of the increasing H_2 concentration.

In summary, from the above discussion of the influence of the various process parameters (C_H^i , t_s , and C_{Mg}^i) upon the formation of pores, it is evident that to minimize porosity formation during DC casting, aluminium manufacturers should strive for high cooling rates and low hydrogen contents. Interestingly, the influence of the restricting growth radius was also very strong, suggesting that the development of alloys that only have tortuous, narrow regions for the pores to grow in will also minimize the percentage porosity. The effect of surface tension is quite significant for this interaction, so if the wetting of the solid by the liquid in the presence of hydrogen could be increased, this should tend to decrease the size and amount, and increase the roundness of pores.

8. CONCLUSIONS

A combined cellular automata and diffusion model has been developed which can predict the formation of porosity in the mushy zone. The model has been applied to some specific problems in solidification of aluminium-silicon and aluminium-magnesium alloys.

The model incorporates the following mechanisms: Nucleation by a stochastic process, diffusion limited growth of the solid, partitioning, and growth of gas pores. The growth of the gas pores may be simplified by assuming the pores are spherical, or by assuming that the restriction by the solid may be approximated by a simple geometry. The competition between the nucleation and growth processes for the excess hydrogen liberated by the partitioning during solidification is the main factor, and so the model predicts the development of the solid phase, within which the gas pores develop.

The competition between nucleation and growth of the solid grains shows the correct behaviour, which replicates the behaviour reported for experiments. Increasing the solidification time increases the grain size, and in the presence of a temperature gradient increases the tendency towards formation of columnar grains. The variability among experiments due to differences in the nucleation can be matched by changing the nucleation input parameters. Alternative models for the distribution of the activity of the nucleation sites can yield essentially identical results; the critical factor is the increase in nucleus density as the undercooling increases compared to the growth rate of the solid tending to extinguish nucleation sites.

By applying multiple linear regression analysis to the results produced by applying the model over a range of parameters, virtual process maps can be developed. Using the assumption of spherical pores, such a map was produced for the effect of solidification time and hydrogen content on the pore size and number in the Al7Si system, assuming constant cooling rates. This map compares well with an experimentally derived map indicating that the important interactions have been encapsulated despite the simplifying assumptions of the model. The

Simulations of the direct-chill (DC) casting of AlMg alloys varying from 2 to 6 wt%Mg show that the interaction of the gas pores and the solid phase is significant during this process. The assumption of spherical pore growth could not predict the behaviour of the experimental process; instead an assumption of increased pressure within the pores allowed the prediction of the experimental behaviour. This system has a longer freezing range than AlSi, and the

initial formation of gas pores is predicted to occur when the overall fraction of solid is high. Therefore, the pores impinge upon the solid when they are small, violating the assumption of spherical pore shape which was sufficient for the Al-Si system.

The scale of most industrially applicable problems is too great to apply this model in a practical fashion directly. However, this limitation may be overcome by studying the model results at the small scale. By using the regression equations to predict the expected results of applying the model, the results can be predicted over a much larger volume. This was done for the effects of solidification time and hydrogen content on the porosity responses during casting of aluminium-silicon alloy and compared to the results of a test wedge casting. The complex pore model was used to generate statistics on the maximum dimension of the pores in addition to the average size and number density statistics. In areas of the casting in which the effect of pressure drop due to shrinkage was not significant, the agreement was quite good.

However, in order to model the interaction between the gas pore and the surrounding liquid and solid metal, some parameters needed to be adjusted, specifically in the equation representing the combined effect of the interfacial energies and the shape of the solid on the gas pressure. Simulations of individual bubbles interacting with simplified geometrical boundaries give some qualitative insight into the relationship in the absence of physical values for the interfacial energies, and indicate that yet more complicated processes are operating.

This serves to underscore the necessity of experimental measurements of the interfacial properties, solubilities, and mobilities, to allow improved predictions from models such as this one.

9. RECOMMENDATIONS FOR FUTURE WORK

There are two distinct categories of activities which proceed logically from the work presented in this Thesis. Firstly, there are a number of questions which may be studied using the model as it is; and secondly there are ways in which the model may be improved and extended to study new problems.

9.1. Suggested uses of the current model

The factorial analysis presented in Section 5.6 is only the first step of an experimental program. By extending the range of the variables studied, and increasing the number of repeated simulations, regression analysis may be used to develop response surfaces [105, 106] thus clearly expressing the interactions between variables. Using a larger number of values for each variable would allow the representation of non-linear interactions, which the factorial analysis appears to indicate. The simulation results should suggest specific casting experiments which should be performed to test the validity.

The behaviour of the pores depends upon the interaction between the rejection of dissolved gas at the solid/liquid interface and the diffusion of gas into growing pores, the pores which nucleate ‘early’ having a significant effect. The model could be used to determine how ‘early’. If a bimodal distribution of nuclei is chosen, the effect on the porosity responses of variations in the distribution could be studied. This would suggest how many low-threshold nuclei must be present to significantly affect the final porosity distribution, or whether increasing the high-threshold nucleus density would minimise the number of large pores produced by low-threshold nuclei.

9.2. Suggested improvements to the model

The studies of the interaction of a bubble with solid surfaces in Section 5.7 rely upon a rough approximation of cylindrical dendrites. However, they indicate the validity of the finite element energy minimisation method of Brakke’s surface evolver [103]. A similar method should be incorporated into the porosity model, allowing the interaction with the generated solid surface to be simulated. This would require constructing a representation of the surface in a continuous and differentiable form from the fraction solid index of each cell. It is possible that methods and existing software developed for the simulation of fluid flow with free surfaces could be adapted for this purpose.

The assumption of constant pressure in the liquid, *i.e.* no shrinkage pressure, limits the experimental situations in which good quantitative agreement with the model can be expected,

as in section 6.3. However, the shrinkage pressure develops as a feature of the geometry of the whole casting, usually of a larger size than can be represented with a grid suitable for modelling the growth of grains and pores. The pressure changes could be included by simulating the fluid flow using Darcy's law at a larger scale with a larger element size, then applying the calculated pressure to a small region modelled by the CA routine. The CA routine would determine the volume change due to pore growth, and the change in volume and fraction solid due to grain growth, and return this information to the large scale model.

The assumption described in section 4.1.5 in which a growth factor is used to determine when new cells are captured by the solid should be investigated further. This could be done by implementing a version of the solidification model which operates at a smaller scale, and determining the averaged fraction solid over several dendrites under various conditions. This information could be used to determine the factor f_s^g as a function of the prevailing conditions rather than a somewhat arbitrary constant.

Each of the comparisons to experimental results has relied upon results available from the literature, or experiments conducted separately for different purposes. An experimental investigation motivated by the model predictions would serve to further validate the model and clarify its weaknesses. Experimentally replicating the results of Section 5.6.1 would be difficult due to the uncertainty of the physical nature of the pore nucleation sites. By varying the melt treatment and mould filling method it may be possible to obtain at least 'high' and 'low' levels of pore nucleation.

As every computer modeller in materials science will agree, more experiments should be done to determine better values for all the physical properties used as inputs to the model.

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APPENDICES

Appendix A. Factorial Experiments

In order to study the effects of multi-parameter interactions on the simulated porosity, a series of modelling experiments was performed using the principles of factorial experimental design.

This method is described in detail by Clarke [107] and other textbooks on statistical experimental design. For these cases, two-level four-factor full factorial designs were used, in which all combinations of two levels of each factor are included. The behaviour of the system is considered to be approximated by a linear equation of all the possible factor interaction terms.

Following the established usage [106, 107] the convention of experimental identification strings (ID strings) is used to designate the treatments (set of applied conditions) and the experimental factors. The lower case letters (**a**, **b**, **c**, **d**) are used to signify the presence of the high level of each of the four factors in an ‘experiment’ (in this case, a model run). The upper case letters (**A**, **B**, **C**, **D**) are used to signify the levels of the factor or combination of factors, normalized so that the high level is 1 and the low level is -1 . Thus the string **ad** represents an experiment in which the first and fourth factors (**A** and **D**) are set to high levels, and the second and third factors (**B** and **C**) are at the low level. In this experiment the interaction factors **AD** and **BC** are high ($-1 * -1 = +1 * +1 = +1$) whereas the factors **AC**, **AB**, **CD**, and **BD** are low, and so on for three- and four-factor interactions. The special string **I** represents all four factors at the low level.

Using this notation, the formula for the linear response y may be written

$$y = \alpha_0 + \alpha_1 \mathbf{A} + \alpha_2 \mathbf{B} + \alpha_3 \mathbf{C} + \alpha_4 \mathbf{D} + \alpha_5 \mathbf{AB} + \alpha_6 \mathbf{AC} + \dots + \alpha_{15} \mathbf{ABCD}, \quad (\text{B-1})$$

and repeating this equation for each of the 16 possible experiments results in the equation for the vector of all responses

$$y_i = \alpha_0 + \alpha_j \bar{\mathbf{A}}_{ij}, \quad (\text{B-2})$$

where i represents all the possible combinations of **a**, **b**, **c**, and **d**, and $\bar{\mathbf{A}}_{ij}$ represents the corresponding matrix of values of **A**, **B**, **C**, **D** and all their combinations. This is represented in Table A-I below (+ represents +1 and $-$ represents -1 , for clarity). In this special case where there is a value obtained for every possible y_i , it is a simple matter to invert the formula and obtain the α_i coefficients. The significance of these coefficients with respect to the

inherent scatter in the responses is estimated by repeating the experiments (in this case repeating the models with different random number seed values) and using an f test to compare the distributions within each factor level with the overall distribution. This was done by following the procedure outlined in detail by Clarke, implemented in a Microsoft Excel spreadsheet, resulting in the graphs forming the bulk of this Appendix. The identification of the factors for each series and the levels used are given in Table A-II. Each of the sets of graphs following is identified by the roman numeral corresponding to the series, and the lower case letter corresponding to the response analysed; *e.g.*, II (a) refers to the results for Series II (7wt % Si) average equivalent spherical radius (R_{av}) results.

On each page, there are five graphs, (i) through (v). Graph (i) shows the model results for each of three repeats of the series, (ii) shows the relative change for each treatment with respect to condition I, (iii) shows the α coefficients, referred to as *factor effects*, (iv) shows the contrast, which is the ratio of the factor sum of squares to the corrected sum of squares of all responses, and represents the proportion of total observed variation which may be attributed to that factor, and (v) shows the significance resulting from the application of the f -test for each factor, comparing the difference from the overall mean due to that factor level with the overall scatter.

The nature of the 'significance' resulting from the f test requires some comment regarding its applicability. The test and the sum-of-squares ratio used embody the underlying assumptions of :

- (1) normal or at least approximately normal distribution of the responses, and
- (2) linear or at least approximately linear behaviour of the interactions.

Therefore a high significance (low p value) has the usual interpretation that the observed difference from the overall mean cannot be explained by the observed scatter within the results, and the often unstated, but nonetheless always present assumption that the behaviour obeys assumptions (1) and (2).

Therefore in deciding the importance of each result, the significance results have been tempered by an examination of the magnitude of the factor effect and the contrast magnitude. An example of what appears to violate these assumptions may be seen in (II-c), the results for the number density of pores N_p in 1 wt%Si. Ten of the factors and interactions appear significant at the 95% level according to the f -test results. Examination of the model responses indicates that this is primarily due to an especially high number of pores in experiment **bcd**

compared to any other experiment. Indeed, the test is not wrong, the level of scatter within each treatment cannot explain this high level – but rejecting the implicit assumption (2) above and suggesting a non-linear interaction (for example a sudden transition in behaviour) seems preferable to requiring ten different interaction terms to explain this behaviour as discussed in Section 5.6.1.

Table A-I. Matrix of normalized factor values.

		A	B	C	D	AB	AC	AD	BC	BD	CD	ABC	ABD	ACD	BCD	ABCD
r00	ab	+	+	-	-	+	-	-	-	-	+	-	-	+	+	+
r01	ad	+	-	-	+	-	-	+	+	-	-	+	-	-	+	+
r02	l	-	-	-	-	+	+	+	+	+	+	-	-	-	-	+
r03	cd	-	-	+	+	+	-	-	-	-	+	+	+	-	-	+
r04	ac	+	-	+	-	-	+	-	-	+	-	-	+	-	+	+
r05	abcd	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
r06	bd	-	+	-	+	-	+	-	-	+	-	+	-	+	-	+
r07	bc	-	+	+	-	-	-	+	+	-	-	-	+	+	-	+
r10	a	+	-	-	-	-	-	-	+	+	+	+	+	+	-	-
r11	b	-	+	-	-	-	+	+	-	-	+	+	+	-	+	-
r12	c	-	-	+	-	+	-	+	-	+	-	+	-	+	+	-
r13	d	-	-	-	+	+	+	-	+	-	-	-	+	+	+	-
r14	abc	+	+	+	-	+	+	-	+	-	-	+	-	-	-	-
r15	bcd	-	+	+	+	-	-	-	+	+	+	-	-	-	+	-
r16	acd	+	-	+	+	-	+	+	-	-	+	-	-	+	-	-
r17	abd	+	+	-	+	+	-	+	-	+	-	-	+	-	-	-

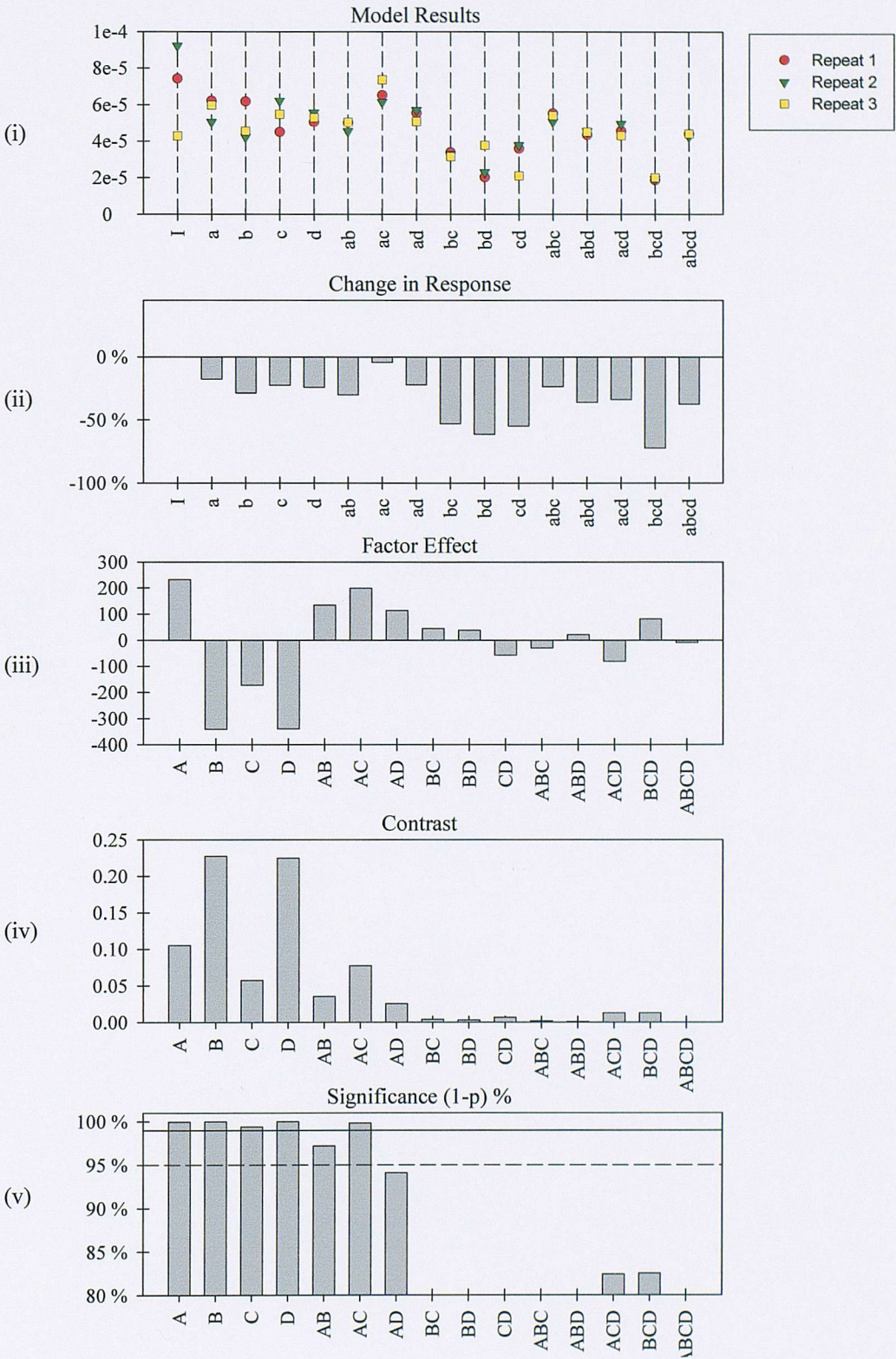
Table A-II. Factor identification and levels used.

Series	Factor	Parameter	Low (-)	High (+)	Units
I	A	N_n^G	1E+09	1E+11 m-3	
	B	ν_g	2.0E-04	5.0E-04 m/s	
	C	C_H^i	0.17	0.43 ml/100g STP	
	D	N_n^p	5E+10	5E+11 m-3	
II	A	N_n^G	1E+09	1E+11 m-3	
	B	ν_g	2.0E-04	5.0E-04 m/s	
	C	C_H^i	0.17	0.43 ml/100g STP	
	D	N_n^p	5E+10	5E+11 m-3	
III	A	ν_g	2.0E-04	5.0E-04 m/s	
	B	G	3200	6300 K/m	
	C	f_s^g	0.75	0.99 ratio	
	D	A_λ	1	2 ratio	

Responses	
(a)	R_a
(b)	L_m
(c)	N_p
(d)	P

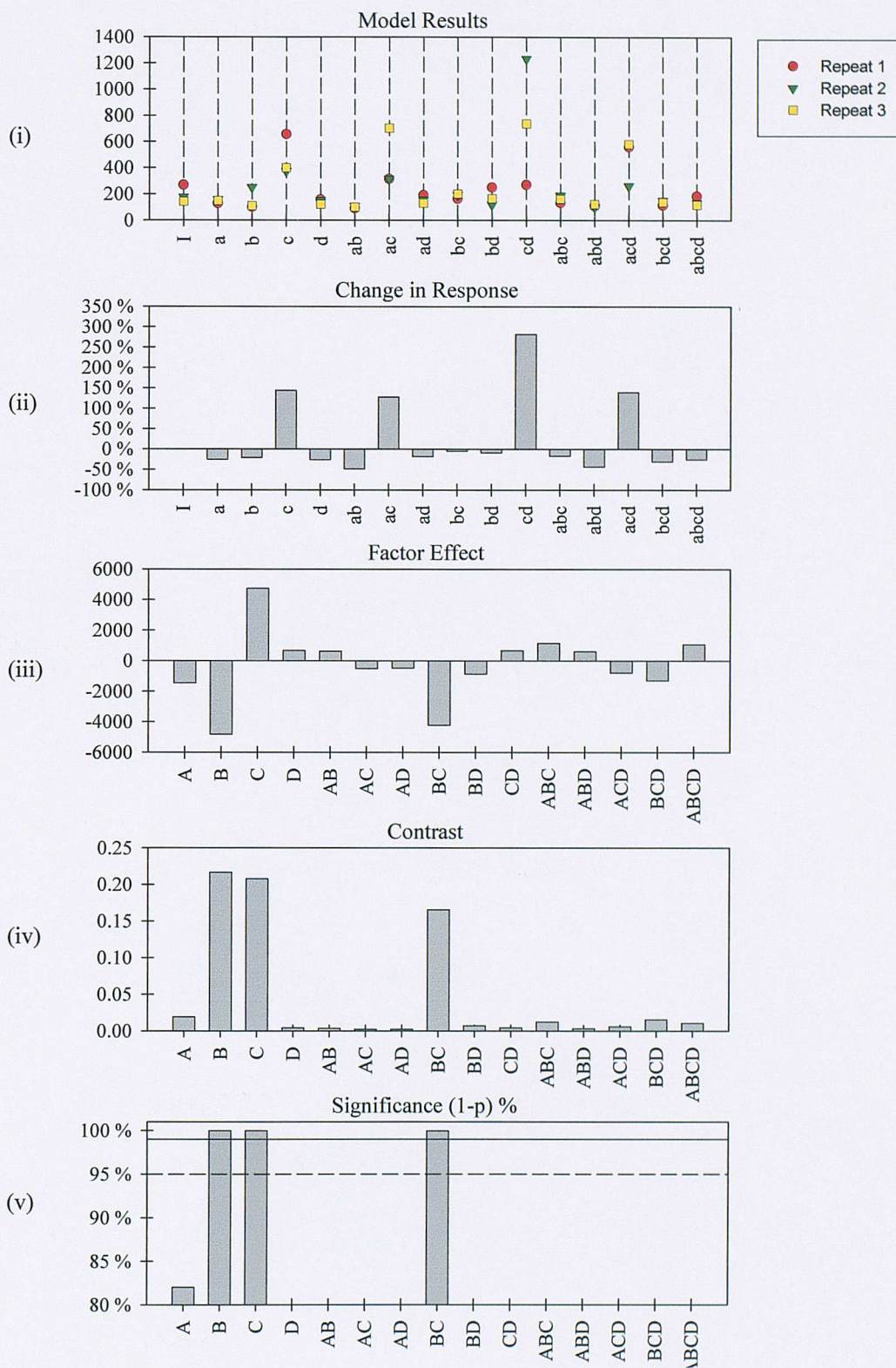
I – Processing and nucleation parameters (a) Average radius (R_{av}) results
1Wt% Si

Factors - $A=N_n^g$ $B=v_g$ $C=C_H^i$ $D=N_n^p$



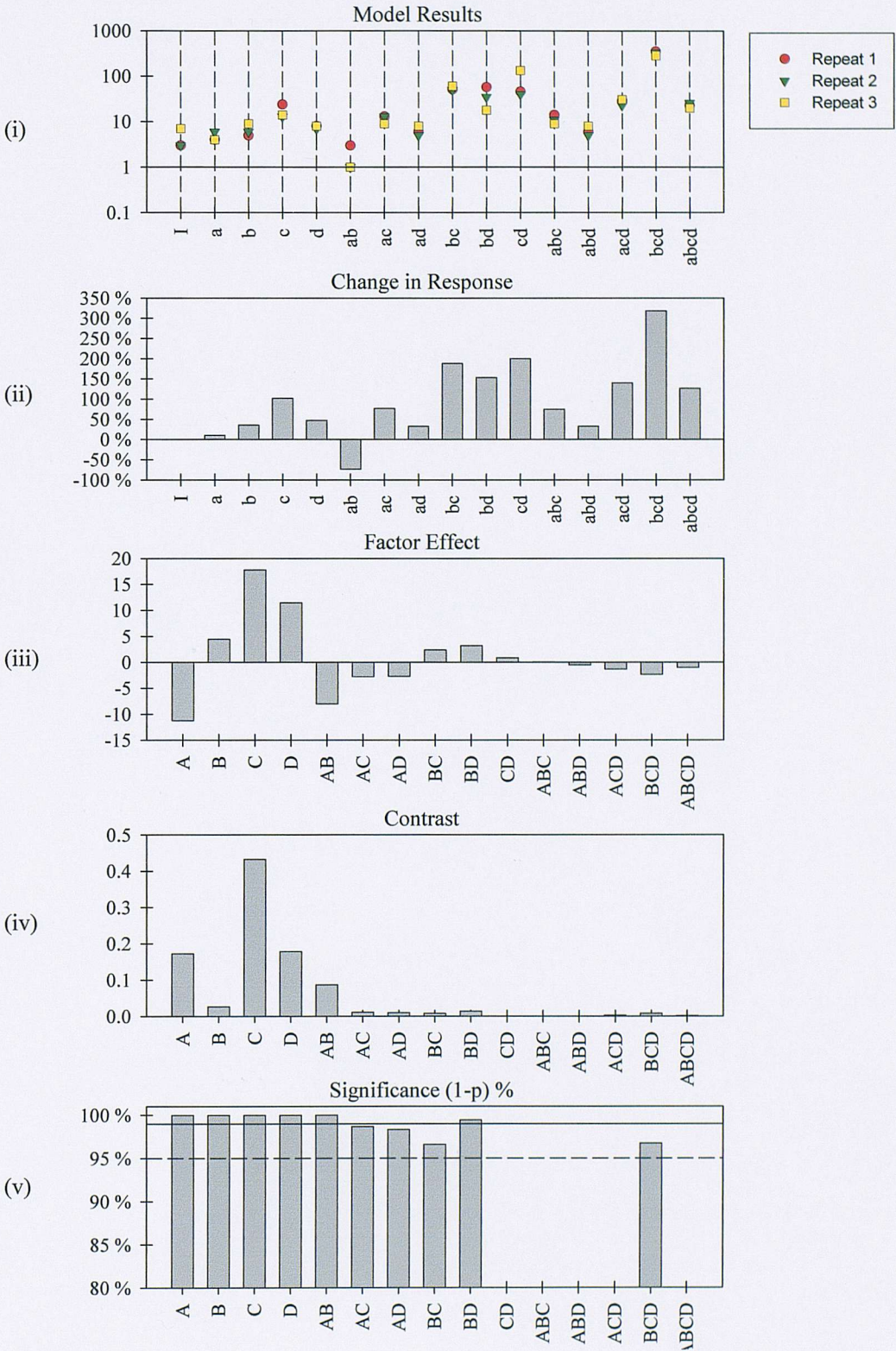
I – Processing and nucleation parameters (b) Max. Length (L_m) results
1Wt% Si

Factors - $A=N_n^g$ $B=\gamma_g$ $C=C_H^i$ $D=N_n^p$



I– Processing and nucleation parameters (c) Number Density (N_p) results
 1Wt% Si

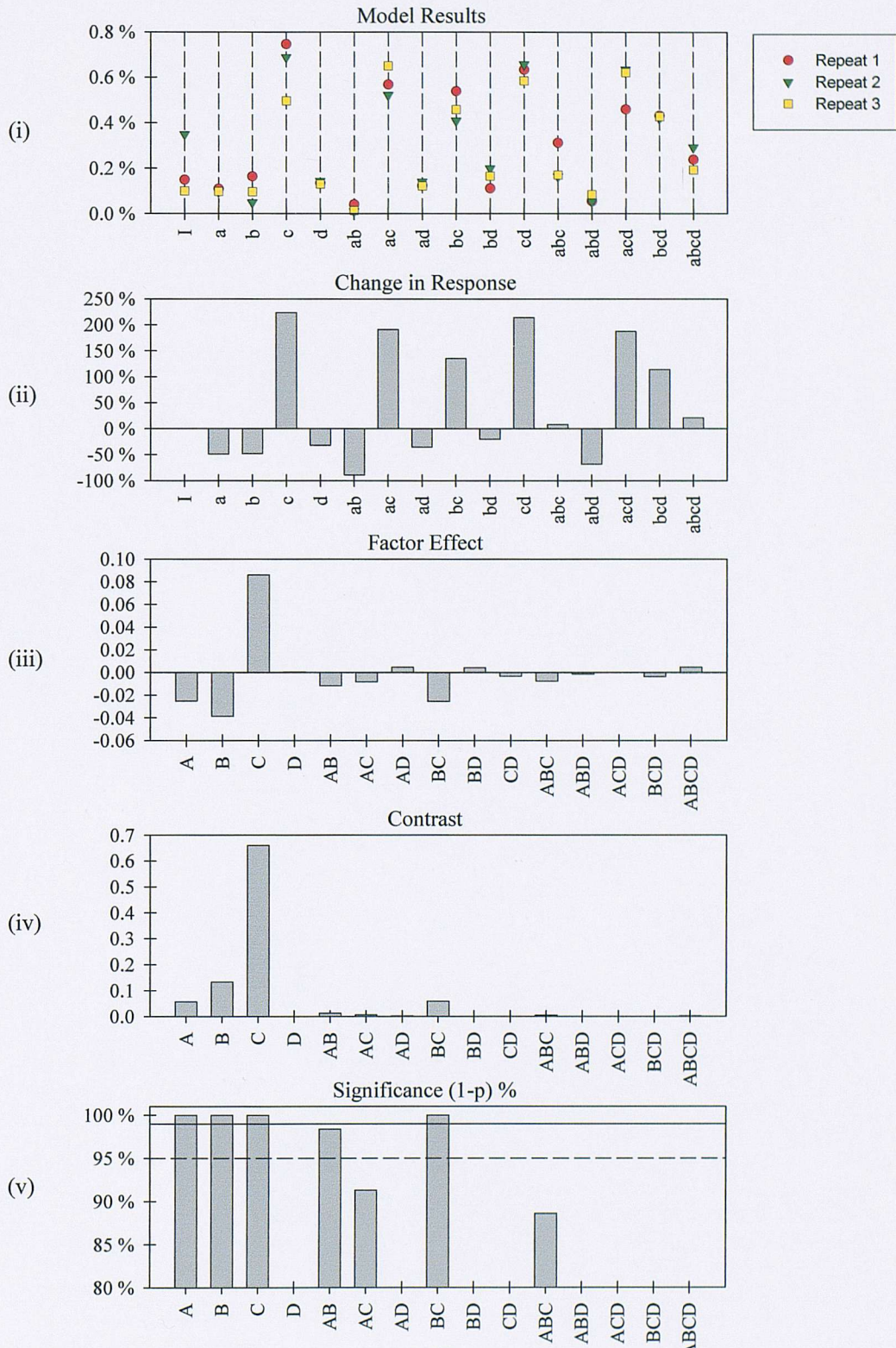
Factors - $A=N_n^g$ $B=v_g$ $C=C_H^i$ $D=N_n^p$



I – Processing and nucleation parameters
1Wt% Si

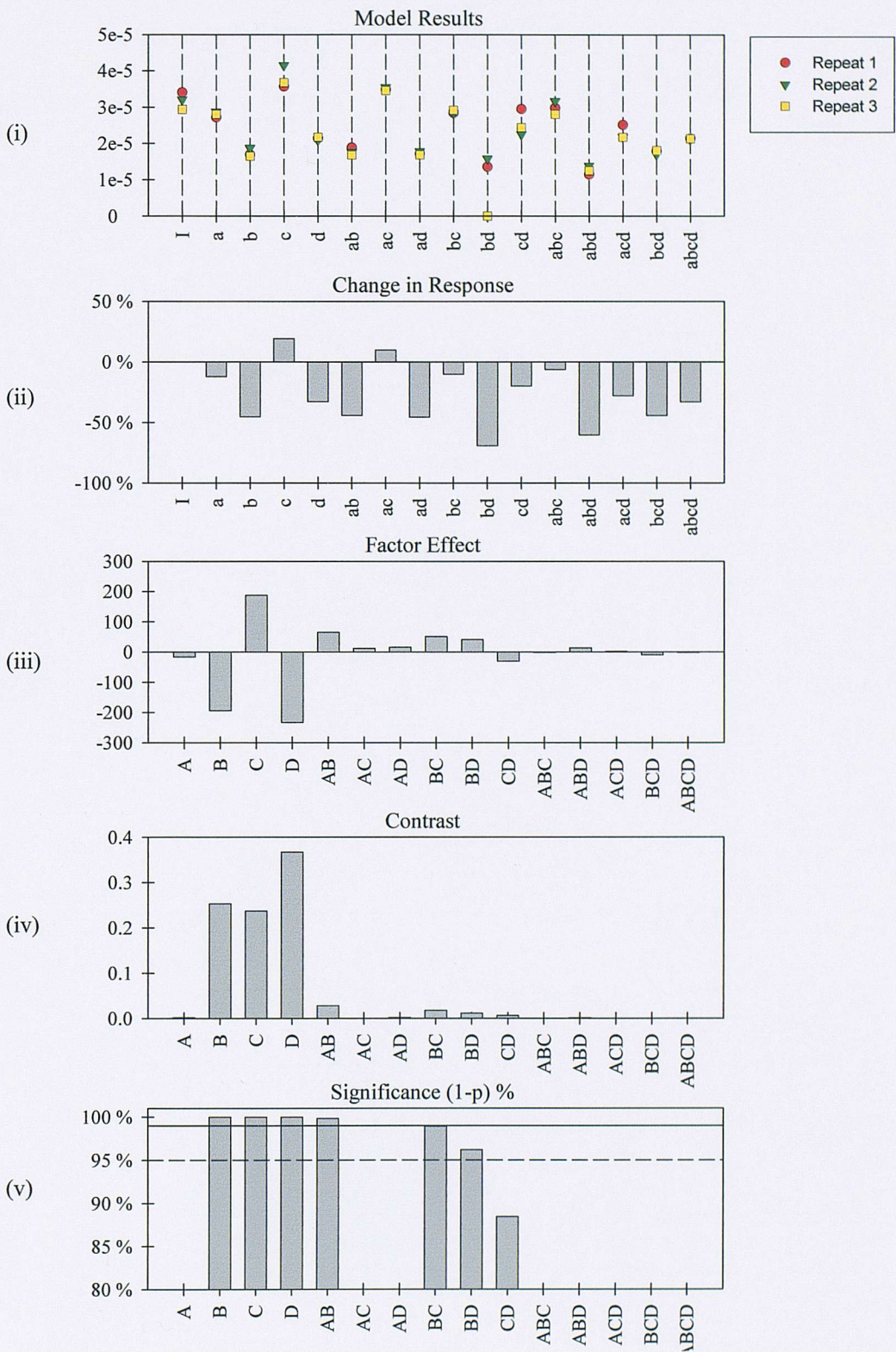
(d) Percentage porosity (P) results

Factors - $A=N_n^g$ $B=v_g$ $C=C_H^i$ $D=N_n^p$



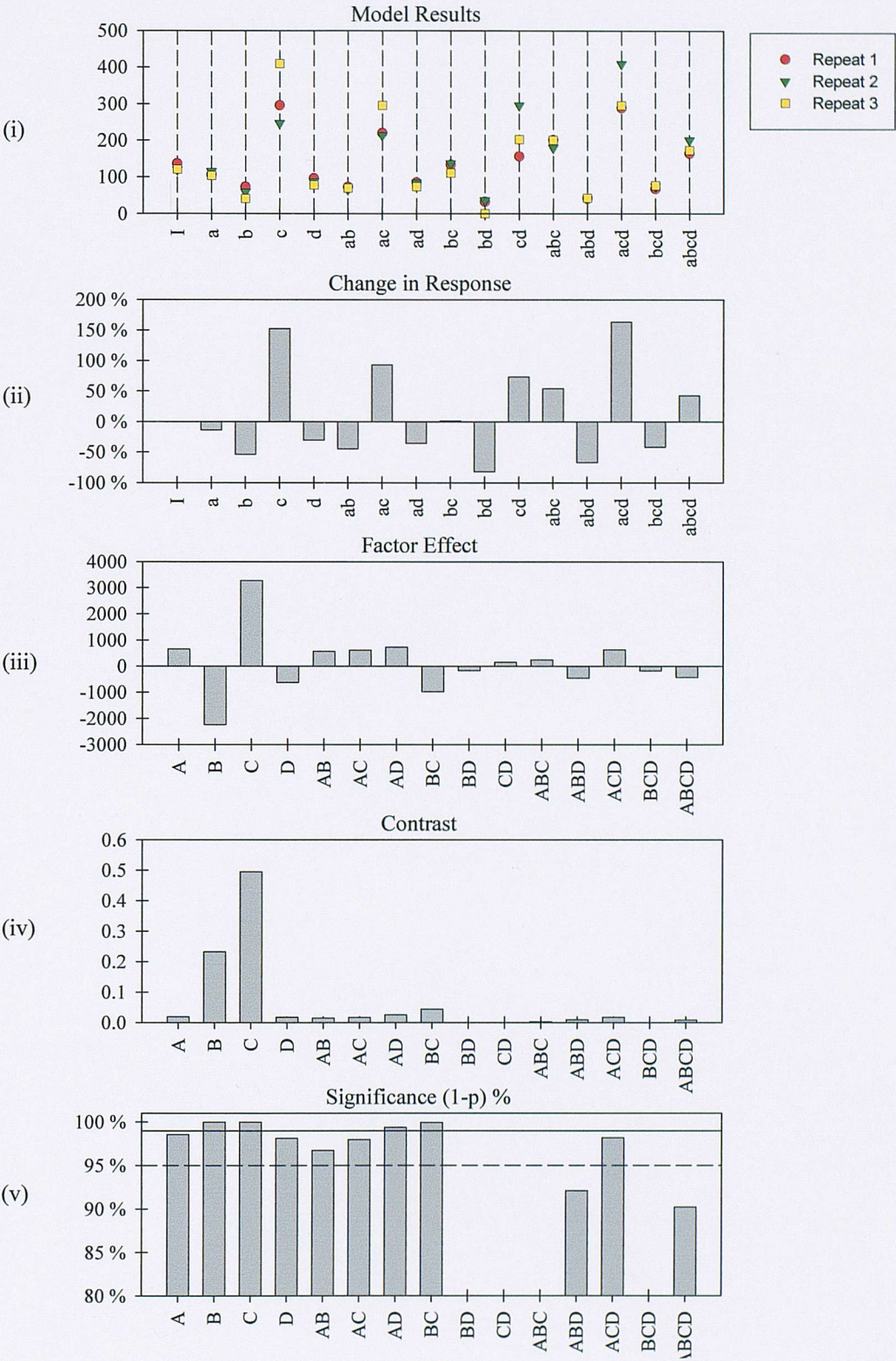
II – Processing and nucleation parameters (a) Average radius (R_{av}) results
7 Wt% Si

Factors - $A=N_n^g$ $B=v_g$ $C=C_H^i$ $D=N_n^p$



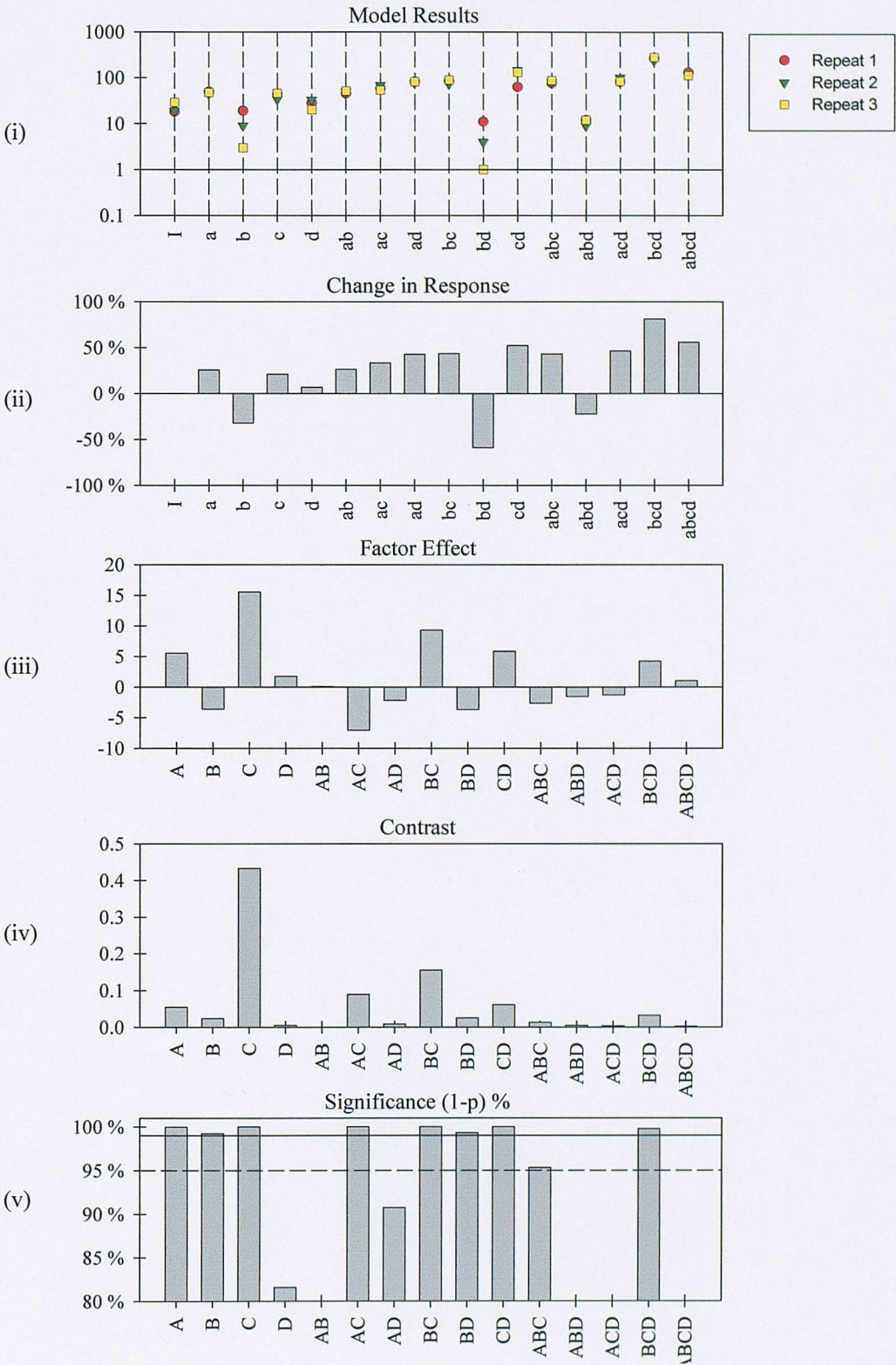
II – Processing and nucleation parameters (b) Max. Length (L_m) results
7 Wt% Si

Factors - $A=N_n^g$ $B=v_g$ $C=C_H^i$ $D=N_n^P$



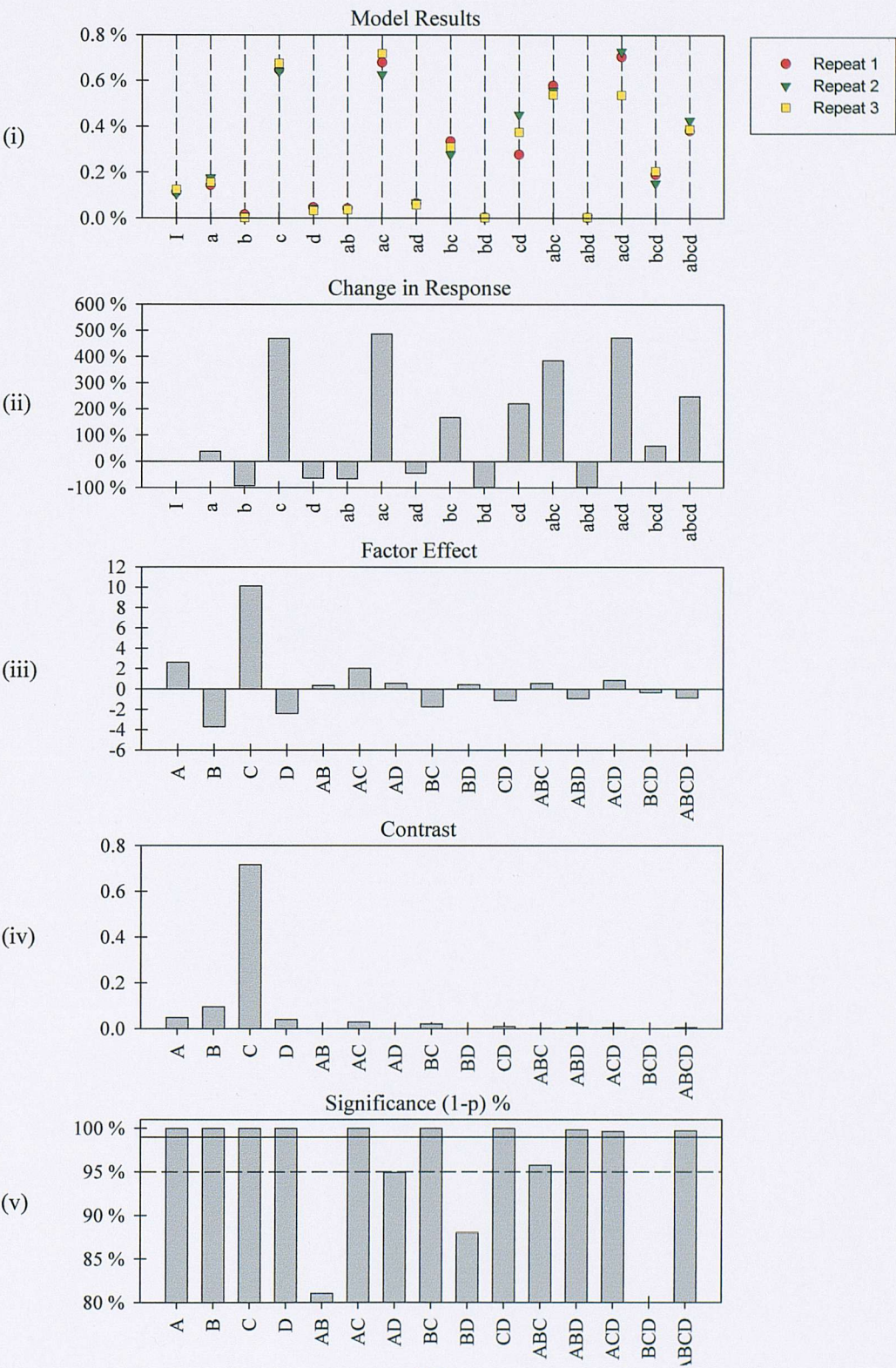
II – Processing and nucleation parameters (c) Number Density (N_p) results
7 Wt% Si

Factors - $A=N_n^g$ $B=v_g$ $C=C_H^i$ $D=N_n^p$

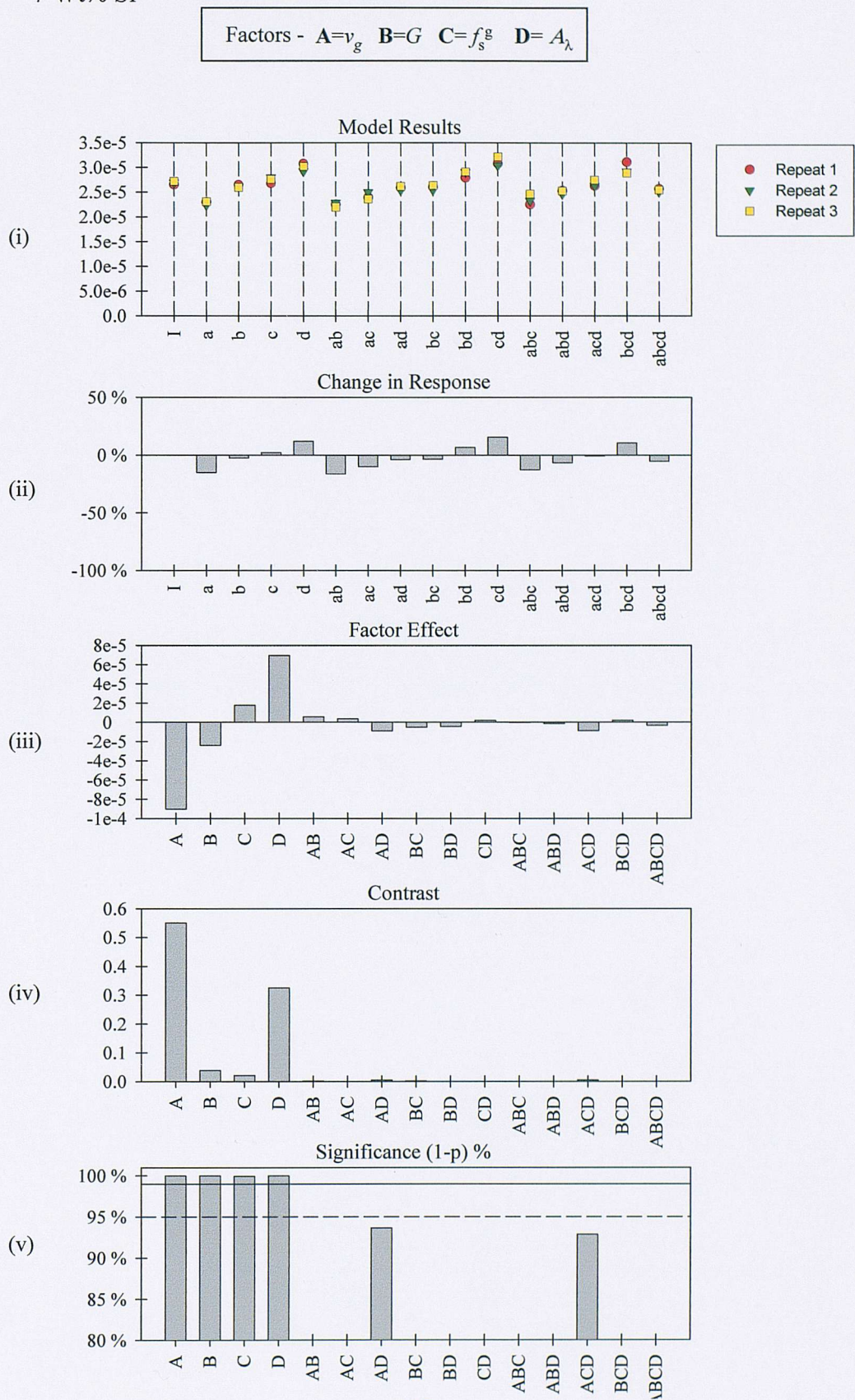


II – Processing and nucleation parameters (d) Percentage porosity (*P*) results
7 Wt% Si

Factors - $A=N_n^g$ $B=v_g$ $C=C_H^i$ $D=N_n^P$

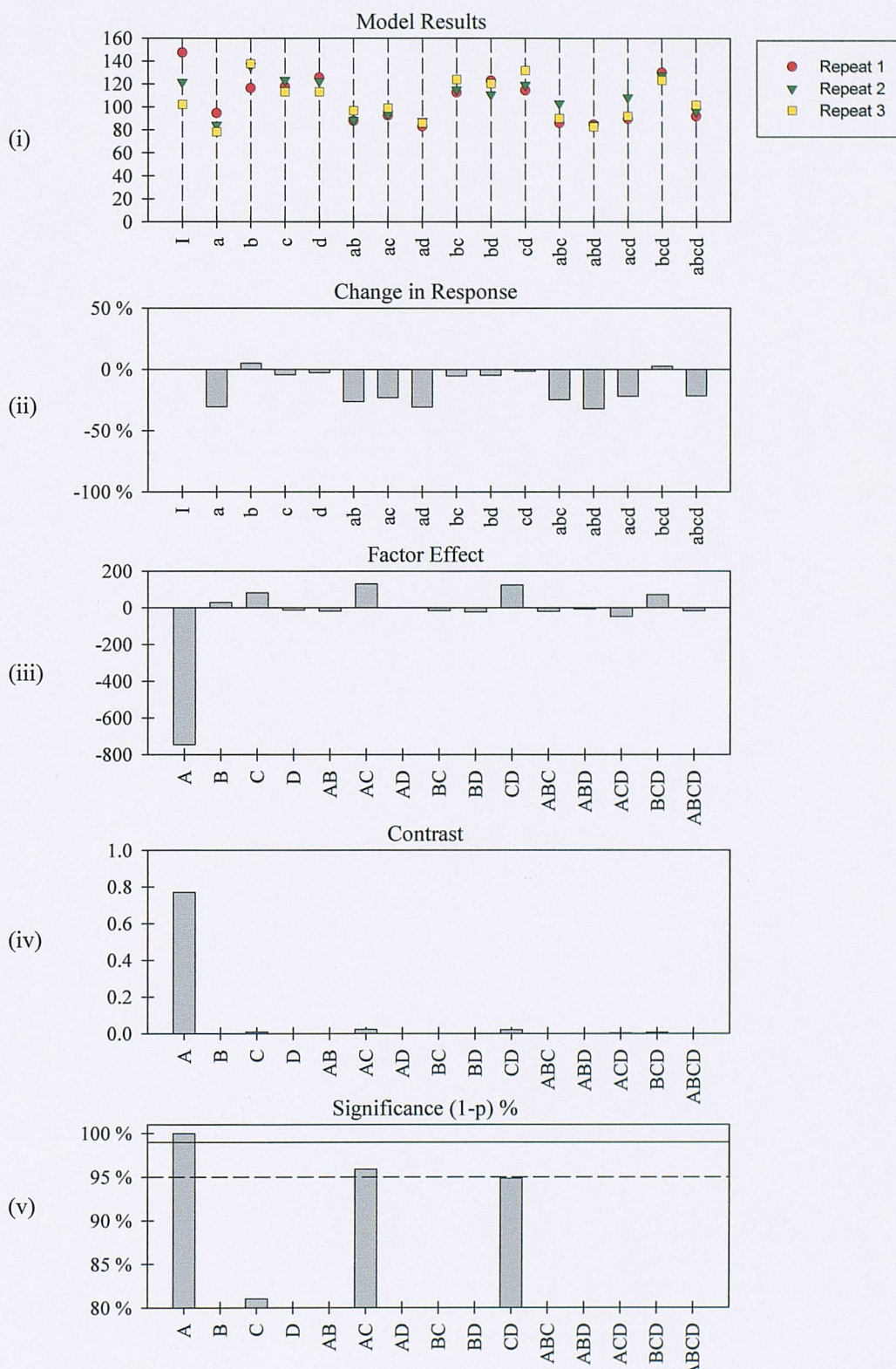


III - Casting and model parameters (a) Average radius (R_{av}) results
7 Wt% Si



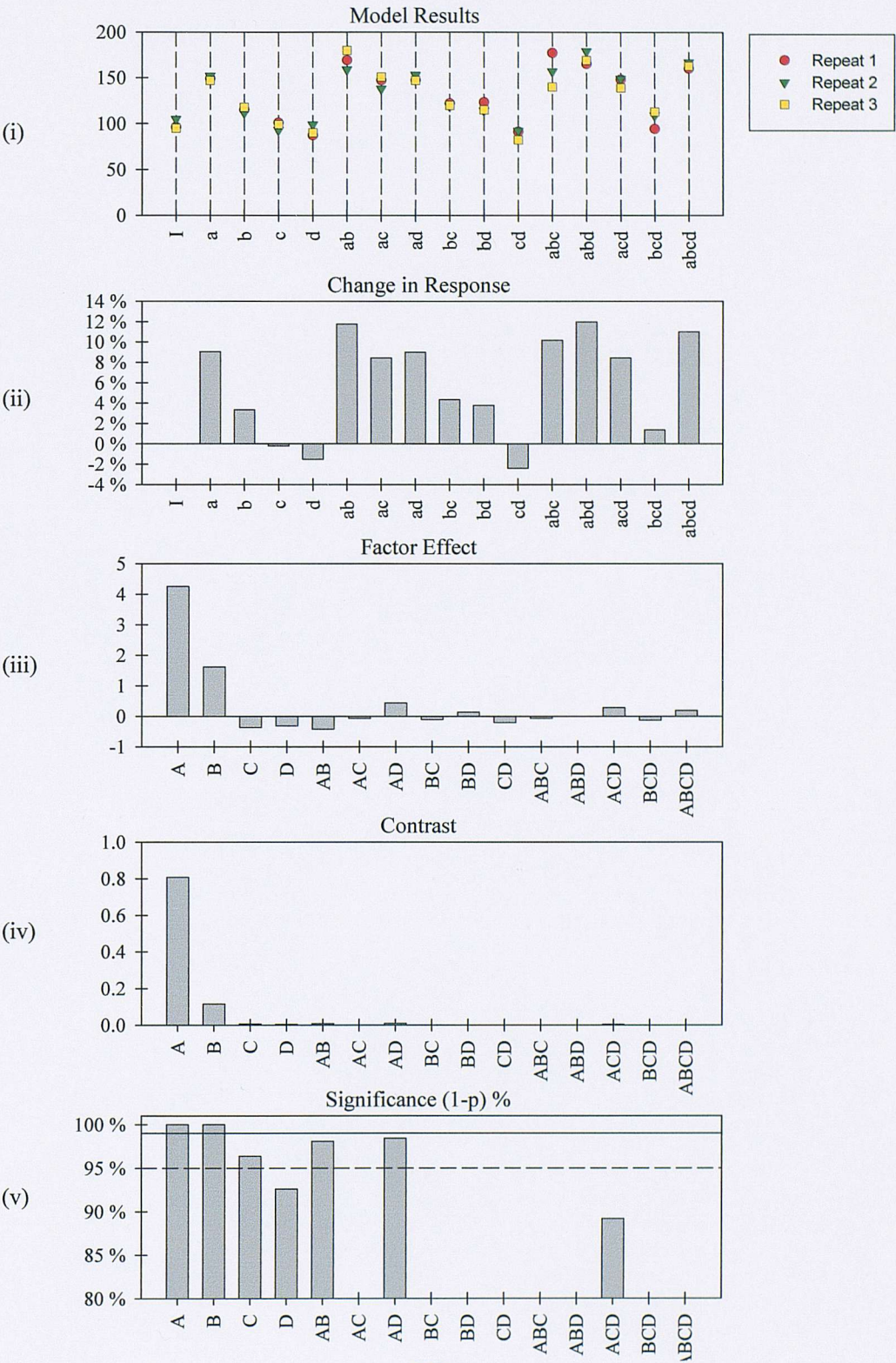
III - Casting and model parameters (b) Max. Length (L_m) results
7 Wt% Si

Factors - $A=v_g$ $B=G$ $C=f_s^g$ $D=A_\lambda$



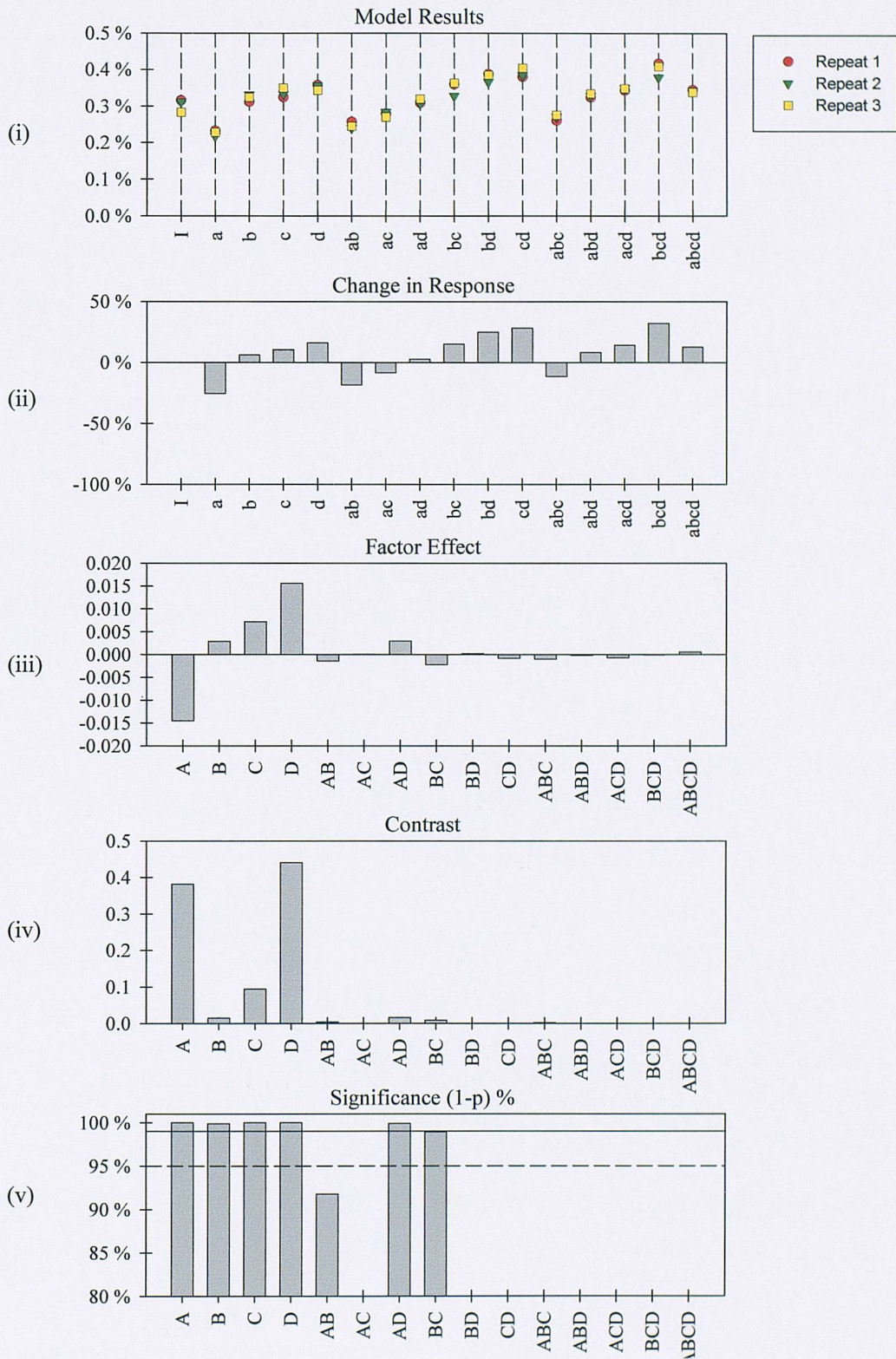
III - Casting and model parameters (c) Number Density (N_p) results
7 Wt% Si

Factors - $A=\gamma_g$ $B=G$ $C=f_s^g$ $D=A_\lambda$



III - Casting and model parameters (d) Percentage porosity (P) results
7 Wt% Si

Factors - $A=\gamma_g$ $B=G$ $C=f_s^g$ $D=A_\lambda$



Appendix B. Statistical Results

In several sections, the statistical significance of changes in a simulated response is referred to. In these cases, the significance is determined by applying either an ordinary Analysis of Variance (ANOVA) or a linear regression analysis which includes a multivariate ANOVA for the selected factors. Unlike the analysis presented in Appendix A, these analyses were carried out using statistical software packages rather than by implementing the analyses directly. The packages used were: DATAPLOT, by James J. Filliben and Alan Heckert^{††}, and Essential Regression, by D. Steppan, J. Werner, and B. Yeater.^{§§}

Table B-I contains the results of applying one-way ANOVA analysis using DATAPLOT to four repeats, with different random number seeds, of the simulations at each of 6 values of Δt . Values of Δt larger than 20 ms were rejected due to overgrowth errors as described in Section 4.1.4. Table B-I (a) shows the overall significance of the change in each response due to changing Δt compared to the change within each level of Δt due to the random factor alone. All the (1-p) significance values are well below the 99% and 95% levels, indicating no observable significance. Table B-I (b) shows the change (effect) in the mean response at each level compared to the overall mean, and no trend is discernable.

Table B-II shows the 4-way ANOVA analysis using DATAPLOT of the results of 108 simulation runs, to determine the effect of the nucleation factors T_c , T_s , N_n , and the distribution shape (0=step, 1=quadratic, 2=Gaussian) at (a) low (0.1 °C) and (b) high (0.5°C) values of the cooling rate (described in Section 4.1.7). The EFFECT column was used for Figure 4-18, this represents the change from the overall mean due to that factor level, after subtracting the effects due to other factors. In set (a) the factors all show high significance, whereas in case (b) only N_n is above the 99% significance level. The factors T_c and T_s are still above the 95% level showing some significance. The factor 'Nuc. Model' representing the type of distribution is well below the 90% level, indicating no observable significance in this case. The trends in the data may also be visualised directly by the box plots shown in Figure B-1. For each level of each factor, the minimum and maximum are indicated by the 'whiskers', the standard deviation by the vertical extent of the box, the mean by the centre of the box, and the number of samples by the width of the box.

^{††} Available from <http://www.itl.nist.gov/div898/handbook/index.htm>

^{§§} Available from <http://www.geocities.com/SiliconValley/Network/1032/>

These computer programs also include very good manuals in electronic form

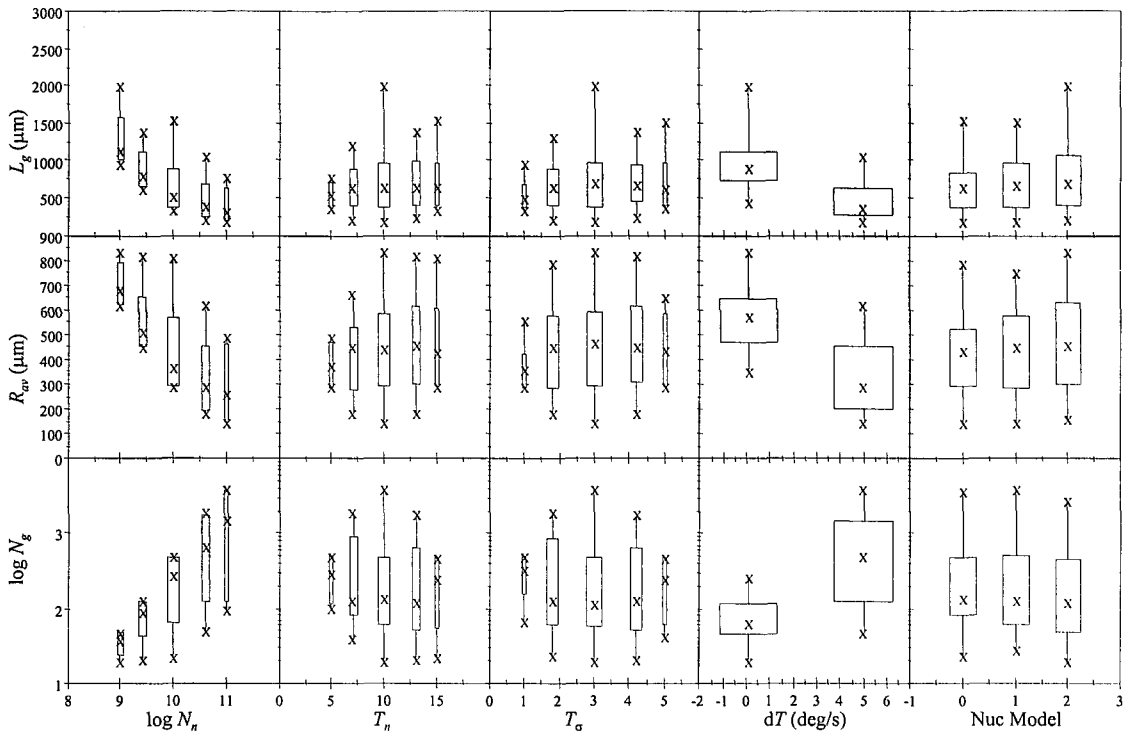


Figure B-1. Box plots indicating the magnitude of effects due to the parameters: N_n , T_c , T_σ , cooling rate and nucleation model. The vertical range of the central box indicates the upper and lower quartiles of each set. The box width represents the relative number of results in each set, and the X's represent the minimum, maximum and mean of each set.

Table B-III shows the multiple linear regression analysis, using Essential Regression, for the 100 simulation experiments (with repeats but excluding simulations which resulted in 0 pores) described in Section 6.3.1. The significance (low 'P values' and 'f-signif') is very good especially since only two or three terms were included in each equation. However, the 'Lack of Fit' (LOF) error is large compared to the pure error, indicating a repeatable trend in the residuals, so it is possible that other terms or a different functional form would improve the fit.

Table B-I. One-way ANOVA results for the effect of altering the timestep Δt on the grain size (after rejecting levels of Δt which resulted in overgrowth warnings).

(a) Significance for each response												
Response	Total DF	Factor DF	Res DF	Total SS	Total MS	Factor SS	Factor MS	Res SS	Res MS	f	(1-p)%	
Ra	23	5	18	1141	50	255	51	886	49	1.03	57.22%	
Lm	23	5	18	119244	5185	22952	4590	96293	5350	0.86	47.25%	
Ng	23	5	18	107	4.63	24.5	4.90	82.0	4.56	1.08	59.35%	

(b) Effects of each level						
Response	Δt (ms)	n	Level MS	Effect	Res. SD Const.	Residual SD Const & Δt
Ra	0.5	4	355.91	5.66	7.04	7.01
	1	4	345.59	-4.66		
	2	4	348.49	-1.76		
	5	4	351.98	1.73		
	10	4	351.06	0.81		
	20	4	348.48	-1.78		
Lm	0.5	4	714.85	43.68	72.00	73.14
	1	4	696.58	25.40		
	2	4	633.75	-37.43		
	5	4	643.91	-27.27		
	10	4	691.69	20.51		
	20	4	646.28	-24.89		
Ng	0.5	4	33.00	-1.75	2.15	2.13
	1	4	36.25	1.500		
	2	4	35.25	0.500		
	5	4	34.25	-0.500		
	10	4	34.50	-0.250		
	20	4	35.25	0.500		

Table B-II. Analysis of the model parameter effects on grain size.

(a) Cooling Rate = 0.1 °C/s						
Source	DF	SS	Mean Sq.			
Total (corr)		53 765113	14436			
Factor	DF	SS	Mean Sq.	f	(1-p)%	Sig.
$\text{Log}N_n$	4	446643	111661	48.18	100.00%	**
T_c	4	91317	22829	9.85	100.00%	**
T_σ	4	52842	13211	5.70	99.90%	**
Nuc. Model	2	94784	47392	20.45	100.00%	**
	Level	N	Mean Sq	EFFECT	SD(EFFECT)	
$\text{Log}N_n(\text{mm}^{-3})$	9.0	3.0	791	220	27.0	
	9.4	12.0	667	96	12.3	
	10.0	24.0	565	-6	7.3	
	10.6	12.0	466	-105	12.3	
	11.0	3.0	434	-137	27.0	
$T_c(^{\circ}\text{C})$	5.0	3.0	475	-96	27.0	
	7.0	12.0	525	-46	12.3	
	10.0	24.0	577	6	7.3	
	13.0	12.0	607	36	12.3	
$T_\sigma(^{\circ}\text{C})$	15.0	3.0	657	86	27.0	
	1.0	3.0	470	-101	27.0	
	1.8	12.0	542	-29	12.3	
	3.0	24.0	584	13	7.3	
	4.2	12.0	591	20	12.3	
Nuc. Model	5.0	3.0	602	31	27.0	
	0	18.0	526	-45	9.3	
	1	18.0	560	-11	9.3	
	2	18.0	627	56	9.3	

(b) Cooling Rate = 0.5 °C/s						
Source	DF	SS	Mean Sq.	f	(1-p)%	Sig.
Total (corr)		53 788899	14884.89			
Factor	DF	SS	Mean Sq.	f	(1-p)%	Sig.
$\text{Log}N_n$	4	786570	196642		556 100.00%	**
T_c	4	5225	1306		4 98.79%	*
T_σ	4	5216	1304		4 98.78%	*
Nuc. Model	2	803	401		1 66.82%	
	Level	N	Mean Sq	EFFECT	SD(EFFECT)	
$\text{Log}N_n(\text{mm}^{-3})$	9.0	3.0	620	303	10.6	
	9.4	12.0	455	138	4.8	
	10.0	24.0	293	-24	2.9	
	10.6	12.0	193	-124	4.8	
	11.0	3.0	152	-165	10.6	
$T_c(^{\circ}\text{C})$	5.0	3.0	289	-28	10.6	
	7.0	12.0	321	4	4.8	
	10.0	24.0	316	-1	2.9	
	13.0	12.0	328	11	4.8	
$T_\sigma(^{\circ}\text{C})$	15.0	3.0	297	-20	10.6	
	1.0	3.0	288	-29	10.6	
	1.8	12.0	322	4	4.8	
	3.0	24.0	316	-1	2.9	
	4.2	12.0	327	10	4.8	
Nuc. Model	5.0	3.0	296	-21	10.6	
	0	18.0	315	-2	3.6	
	1	18.0	314	-3	3.6	
	2	18.0	322	5	3.6	

Table B-III

Statistical summary for the regression of CA porosity responses.

(a) Equation 6-2 $\text{LuAvR} = b_0 + b_1 \cdot \text{LnTsC} \cdot \text{CiFu}$;							Source	SS	SS%	MS	F	F Signif	df	R	R ²	R ² adjusted
P value	Std Error	-95%	95%	t Stat			Regression	13.13	86	13.13	561.80	1.98e-41	1	0.926	0.857	0.855
b0	2.94	4.10e-87	0.038	2.87	3.02	77.75	Residual	2.20	14	0.02			94			
b1	0.91	1.98e-41	0.038	0.83	0.99	23.70	LOF Error	2.17	14 (99)	0.03	17.73	5.18e-08	78			
							Pure Error	0.03	0 (1)	0.00			16			
							Total	15.33	100				95			
(b) Equation 6-3 $\text{LnMaxL} = b_0 + b_1 \cdot \text{LnTsC} \cdot \text{CiFu}$							Source	SS	SS%	MS	F	F Signif	df	R	R ²	R ² adjusted
P value	Std Error	-0.95	0.95	t Stat			Regression	38.95	81	38.95	401.71	1.05e-35	1	0.900	0.810	0.808
b0	3.94	2.19e-70	0.077	3.79	4.09	51.11	Residual	9.12	19	0.10			94			
b1	1.57	1.05e-35	0.078	1.41	1.72	20.04	LOF Error	8.63	18 (95)	0.11	3.65	2.72e-03	78			
							Pure Error	0.48	1 (5)	0.03			16			
							Total	48.07	100				95			
(c) Equation 6-4 $\text{PctPor} = b_0 + b_1 \cdot \text{CiFu} + b_2 \cdot \text{LnTsC} \cdot \text{CiFu}$							Source	SS	SS%	MS	F	F Signif	df	R	R ²	R ² adjusted
P value	Std Error	-0.95	0.95	t Stat			Regression	16.96	91	8.48	471.51	2.09e-49	2	0.954	0.910	0.908
b0	-0.37	4.45e-13	0.044	-0.46	-0.28	-8.421	Residual	1.67	9	0.02			93			
b1	4.04	7.30e-33	0.219	3.60	4.47	18.46	LOF Error	1.62	9 (97)	0.02	6.94	4.56e-05	77			
b2	0.18	2.52e-04	0.048	0.09	0.28	3.807	Pure Error	0.05	0 (3)	0.00			16			
							Total	18.63	100				95			

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