THE INFLUENCE OF TiN PARTICLES ON THE NUCLEATION OF SPURIOUS GRAINS DURING SINGLE CRYSTAL CASTING OF SUPERALLOYS

by

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to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

May 2003

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Abstract

Spurious grains are defects that arise in single crystal turbine blades of superalloys. Because they can act as favorable locations for crack initiation and in-service failure, they often lead to blades being rejected. Although spurious grains in single crystal castings may nucleate by many mechanisms, strong but indirect evidence exists that the presence of nitride and oxide inclusions can reduce the amount of undercooling necessary for grain nucleation and hence increase the formation of spurious grains. In this project, this hypothesis, in regard to nitride inclusions, was tested directly by experiments. In the experiments, the nucleation of spurious grains was “turned on” by providing nitride inclusions at the liquidus temperature, in alloys where the oxide content is constant and known. Solidification front undercooling was varied by changing the solidification velocity in order to estimate the critical undercooling for nucleation. A thermal model of the single crystal casting process was developed to analyze the thermal history of the casting process. Equiaxed grains and columnar to equiaxed transitions (CET) were observed in alloys with a nitrogen content much higher than the saturation solubility, in those cases where the solidification front undercooling was in excess of the critical undercooling. Experiments were done on samples with a simple shape. Dendrite tip undercoolings were estimated by using the well-known KGT model using the pseudo binary approximation. The influence of nitrogen content on the nucleation kinetics was quantitatively studied based on theories given in the literature.
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<tr>
<td>$A$</td>
<td>Kinetics Parameter</td>
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<td>$A_j$</td>
<td>Atomic Mass of the $j$-th Component</td>
</tr>
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<td>CET</td>
<td>Columnar-to-Equiaxed Transition</td>
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<td>Solute Concentrations at the Interface in the Solid</td>
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<tr>
<td>$C_i^*$</td>
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<td>Directionally Solidification and Quench</td>
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<td>Liquid Diffusion Coefficient ($\text{m}^2/\text{s}$)</td>
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<td>$G_2^*$</td>
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<td>Dendrite Growth Kinetics of Kurz, Giovanola and Trivedi</td>
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<tr>
<td>M</td>
<td>An Alloy</td>
</tr>
<tr>
<td>Me</td>
<td>A Pure Metallic Solvent</td>
</tr>
<tr>
<td>$m, m_i$</td>
<td>Slope of the Liquidus (K(wt%)$^{-1}$)</td>
</tr>
</tbody>
</table>
n Number of Components in the Alloy

n Kinetics Parameter

\( N_0 \) Nucleation Site Density (m\(^{-3}\))

[\%N] Solubility of Nitrogen (in Mass Fractions) at \( P_{N_2} = 1 \) atm, and the Temperature 1873 K in an Alloy M

[\%N]_{Me} Solubility of Nitrogen (in Mass Fractions) at \( P_{N_2} = 1 \) atm, and the Temperature 1873 K in a Pure Metallic Solvent Me

\( n_{max} \) Total Number of Nucleation Sites Available

\( P_c \) Péclet Number

\( R \) Gas Constant

\( R_{\text{max}} \) Maximum Tolerated Size of an Isolated Spurious Grain

\( \Delta S^o \) Standard Entropy

SX Single Crystal

S/L Solid/Liquid

\( T_L \) Liquidus Temperature

\( T_S \) Solidus Temperature

TCP Topologically Close Packed Phases

\( \Delta T \) Solidification Front Undercooling (K)

\( \Delta T_c \) Solutal Undercooling (K)

\( \Delta T_k \) Kinetic Undercooling (K)

\( \Delta T_r \) Dendrite Tip Curvature Undercooling (K)

\( \Delta T_t \) Thermal Undercooling (K)

\( \Delta T_0 \) Equilibrium Solidification Interval at the Composition \( C_0 \) (K)
<table>
<thead>
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<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
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<td>$\Delta T_N$</td>
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</tr>
<tr>
<td>$V$</td>
<td>Solidification Rate ($\text{ms}^{-1}$)</td>
</tr>
<tr>
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Chapter 1 Introduction

The efficiency of modern aircraft engines and advanced land base gas turbines is closely linked with the turbine operating temperature, and particularly the temperature at the turbine inlet. The high-pressure turbine blades and vanes, located in this hottest section of the engine, are made from Ni-based or Co-based superalloys. These components typically have a complex geometry, which includes internal air-cooling passages to facilitate their operation in gas temperatures that exceed the incipient melting point of the alloy. The introduction of single crystal (SX) blades, which eliminates the internal grain boundaries, has improved the durability and strength of these critical parts allowing increased temperatures and efficiencies to be achieved.

One of the major problems encountered during SX casting is the formation of spurious grains. The spurious grains arise from the nucleation and growth of an undesired grain in the body of the blade (airfoil, root), or at specific locations such as platform ends. For SX alloys, the introduction of a grain boundary is particularly harmful as no metallurgical grain boundary strengthener is added in the design of the alloy composition. The spurious grains can thus act as weak spots leading to creep rupture and crack initiation resulting in in-service failure. In general, the occurrence of spurious grains can be reduced in a given alloy by increasing temperature gradients ($G$) at the solidification front and reducing solidification rates ($V$). The propensity to form these stray grains scales with component geometry and becomes higher in the large blades used in land-based industrial gas turbines (IGT’s), where it
is more difficult to maintain large temperature gradients at the solid/liquid interface.

Spurious grains in blade casting can originate from a number of sources including at abrupt changes in blade cross-section (air foil root and platform) and in association with freckles (vertical chains of small equiaxed grains stemming from thermo-solutal convection). In addition, manufacturing experience has shown that there is occasionally no obvious source. One hypothesis is that nitrides and oxides present in the melt might promote spurious grain formation by reducing the amount of undercooling necessary for nucleation to the point that these inclusions become the principle nucleating factor in SX castings. Nitrides have been known for some time to be effective nucleating agents in certain cast steels. For example, studies have revealed that TiN is an effective nucleating agent in ferritic stainless steels but not in austenitic stainless steels. The difference in the response between the two steels is believed to be due to the extent to which there is lattice mismatch between TiN and the BCC (ferritic) and FCC (austenitic) structures. Some studies on the effects of nitrides and oxides on the heterogeneous nucleation of spurious grains in superalloys have been completed. The results, however, while tending to support the hypothesis, are not conclusive.

The nucleation and growth of a spurious grain is mechanistically very similar to the more general columnar-equiaxed transition (CET) seen in many conventional casting processes. The CET has been investigated for binary alloys as well as for multi-component superalloys for a long time and hence the associated literature provides a good repository of information for study. Several models have been suggested to calculate the critical undercooling values for CET and based on these models many criteria have also been
proposed. In addition, many crystallographic parameters influencing nucleation are also available in the literature.

This project proposes to test the hypothesis that nitride inclusions can cause nucleation in Ni-based superalloys directly by conducting experiments in which spurious grain nucleation would be "turned on" by the single effect of providing nitride inclusions at the liquidus temperature, in alloys where the oxide content is constant and known. A series of experiments involving the use of the Bridgman-type furnace and a directional solidification and quench (DSQ) furnace have been accomplished. A thermal model of the single crystal casting process was developed to fill in gaps in the thermocouple data in order to link solidification conditions existing at the S/L interface to changes in solidification morphology. The critical undercooling values for the nucleation of spurious grains were calculated for alloys with different nitrogen content.
Chapter 2 Literature Review

Spurious grain formation in SX blades is linked to the local solidification conditions ($G$ and $V$ at the solid/liquid interface), to alloy chemistry and to mould face-coat chemistry. Non-metallic inclusions like nitrides and oxides may also play a related role. The literature pertaining to these various factors has been reviewed to provide a foundation for completion of this study.

2.1 Single Crystal Superalloys

Improvements to materials and casting techniques over the last 50 years have enabled superalloys to be used in more and more severe environments. For example, equiaxed castings were used in the 1940s initially. Subsequent development in casting technology included directionally solidified (DS) materials in the 1960s, and finally single crystals (SX) in the 1970s [1]. In Ni-based alloys, the natural growth direction for dendrites is in the <100> crystallographic direction. SX castings are produced by selecting a single grain, via a grain selector or SX seed, and allowing the single grain to grow to encompass the entire part.

Typical compositions of single crystal alloys of three generations are shown in Table 2-1 [2, 3, 4, 5], Table 2-2 [2, 3] and Table 2-3 [3]. The first-generation alloys were slightly modified versions of the multi-crystal directionally solidified alloys, with the grain boundary strengthening elements removed. The second-generation alloys are typically those whose chemistries have been carefully engineered for the single crystal application, and often
contain high levels of W, Ta, and Re. In the third-generation alloys, the rhenium content has been increased to up to about 6 wt% in order to further improve the high temperature capability. Collectively, alloy additions often comprise over 30% of the weight of a single crystal alloy. Consequentially, significant segregation of the solute elements can occur during solidification, with the associated potential for constitutional super cooling ahead of the dendrite tips.

The exceptional properties of SX components are due to:

1. The elimination of grain boundaries.

2. The elimination of grain boundary strengtheners such as C, B, Si, and Zr. (The elimination of these additions raises the single crystal's melting point. By increasing the alloy's melting point, the homogenization heat-treat temperature can be increased without fear of incipient melting, thus allowing for more complete solutionizing of the γ' and thereby increasing alloy strength and maximum use temperature.)

3. The low modulus associated with the <100> directions enhances thermal mechanical fatigue resistance in areas of constrained thermal expansion—particularly turbine vanes. (The lack of grain boundaries coupled with the lower modulus can result in 3-5-fold improvement in fatigue rupture life.)

The growing market for large land-based turbines for power generation has resulted in increased use of nickel-based superalloys in recent years. Presently, this application accounts for approximately 15% of superalloy demand according to a marketing report published in 1999 [6]. There are principally three differences between relatively small aero-engine single crystal blades and their equivalent for use in land based gas turbines which could impact adversely on their ability to be cast as a single crystal [7]. Firstly, the size of blade roots and platforms are larger than in the aero-engine case, and secondly, there are significant
differences with respect to their alloy content. The effect of increased size is to reduce axial
temperature gradients and increase transverse temperature gradients both of which tend to
increase the tendency to form spurious grains. Insofar as the chemistry is concerned, the SX
alloys for use in land base turbines will require a greater degree of resistance to oxidation
owing to the differences in the fuels used. The composition of typical SX alloys used in land
base turbines were given in Table 2-4. As can be seen, there is a substantial increase of Cr
content compared to SX alloys used in aero-engines.

2.2 The Spurious Grains

Grain defects that can often be found in a SX casting are: low angle grain boundaries,
high angle grain boundaries, freckles, spurious grains, stray grains, slivers. (The low angle <
10° grain boundary is usually acceptable for many SX parts). These defects are defined as
follows:

Low angle grain boundaries - refers to a second or third grain that forms
having an orientation within approximately 10° of the primary grain, or stress angle.

High angle grain boundaries - refers to second or third grains; however, with
an orientation in excess of 10° to the stress axis angle.

Freckles - refers to chains of fine, randomly oriented equiaxed grains. The
chain of equiaxed grains is usually oriented in the casting direction and the
composition is shifted toward the alloy eutectic.

Both spurious grains and stray grains - are grains nucleated in a SX part.
While stray grains usually refer to fine equiaxed grains with a random direction and
appear on the surface, thus have a different nucleation mechanism related to surface
reaction [8]. However, it should be noted that the difference between these two terms
is not distinctive, and they are used indiscriminately by many people.
Slivers — refers to secondary narrow columnar grains that usually appear on the surface of the castings. The occurrence of slivers has been found to be strongly related to the surface defects and nonmetallic inclusions [9].

The formation of spurious grains is one of the major problems encountered during the SX casting process. The spurious grains arise from the nucleation and growth of an undesired grain in the body of the blade (airfoil, root etc.) or at specific locations such as platform ends (Figure 2-2). For SX parts, these defects are particularly harmful as no metallurgical grain boundary strengthener is added in the alloy. The spurious grains can thus act as a favorable location for crack initiation and in-service failure. Transverse grain boundaries are not acceptable in single crystal castings. Consequently, in many instances they are considered as a fatal defect requiring that the SX part be scrapped. A number of recent studies on grain related defects appear in the literature [7, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21], which will be reviewed later in this chapter following the presentation of additional background material.

2.3 SX Casting Process and the Nucleation of Spurious Grains

2.3.1 SX Blade/Vane Casting Process

Face-centred-cubic (FCC) and body-centred-cubic (BCC) dendrites grow preferentially in the <100> crystallographic orientation. Under certain solidification conditions (generally high gradient and low solidification rate) initially randomly oriented grains will align themselves with the direction of heat flow through a process of competitive elimination. (Those grains that have the <100> direction aligned with the direction of heat
flow are required to grow at a lower velocity to keep up with the liquidus isotherm and hence are less undercooled. Consequently, they can branch more efficiently and quickly occlude adjacent unaligned grains.) The SX casting processes take this selection process one step further and seeks to eliminate all but one of the grains.

The main industrial process used to directionally solidify single crystal superalloys is based on the so-called Bridgman method as shown in Figure 2-1 [22]. Molten alloy is poured into a ceramic shell mold that has been preheated to a temperature above the liquidus of the superalloy. The preheated shell mold is open at the bottom and sits on a water-cooled copper chill plate. The molten superalloy solidifies upon contact with the copper chill to form a thin layer of equiaxed grains. After solidification has started, the water-cooled chill plate is lowered gradually, withdrawing the ceramic shell mold filled with molten superalloy, from the heated furnace. Heat loss is controlled by radiation from the shell mold to the cold vacuum chamber walls. A baffle can be placed at the bottom of the furnace as shown in Figure 2-1 to minimize radiative exchange between the hot and cold zones of the furnace thus increasing the thermal gradient at the S/L interface.

Solidification begins in the starter block with an equiaxed chill layer that quickly organizes into a columnar-grained structure consisting of an array of vertically aligned grains. In some of the industrial processes, a single crystal casting is obtained by inclusion of a helical constriction above the starter block region of columnar grains. The helix acts as a filter and only permits a single grain to emerge. The selected grain then fills the shell cavity resulting a <001> oriented single crystal casting. As previously indicated the primary
orientation of a single crystal, <001>, is required to be within 10° from the main stress axis of a blade to ensure a uniformly low modulus. In an alternate version of this process, a seed crystal replaces the helical grain selector. With the use of seed crystals any primary or secondary orientation can be achieved. The seed crystals are typically of the desired alloy or one with an equivalent or higher melting temperature. The orientation of the seed crystal will be repeated in the casting. The seed sits on the chill in a reduced section of the mould. The temperature at the top of the seed is controlled so that the top of the seed crystal melts without melting the rest of the seed, thereby allowing the molten alloy in the mold cavity to solidify on the seed crystal guaranteeing the same orientation in the casting as in the seed.

As previously described, the propensity to form spurious grains scales with the size of the component being cast. Demand for a more efficient single crystal casting process, especially for the casting of large size single crystal blades for land base gas turbines, has led to renewed interest in the Liquid Metal Cooling Process (LMC) [23] as well as development of a new technique, the so called Gas Cooling Casting (GCC) [24]. The LMC process uses a liquid metal such as Al or Sn as a coolant, whereas the GCC process uses an injected inert gas as a coolant. Both processes offer important advantages over the conventional solidification process: 1) increased axial gradient at the S/L interface by a factor of two or more [24, 25], and 2) decreased transverse gradient – in the conventional process, radiation cooling in a cluster of blades is only effective on the cluster periphery.

The increased axial thermal gradient offers a two-fold advantage; firstly, it can potentially eliminate spurious grains in larger blades; secondly, it offers the potential to also
increase the withdrawal rate (solidification rate), while maintaining a mono-crystalline casting. An increase in cooling rate by a factor of four or more will produce a general improvement of the microstructure including, smaller dendrite arm spacings, reduced inter dendritic segregation, suppressed formation of low-melting equilibrium phases like γ-γ'-eutectic, and reduced interdendritic porosity. Tensile, creep and fatigue properties are consequently enhanced. The reduced transverse gradient can help diminish the likelihood of stray grain nucleation in reentrant corners (the term reentrant corner refers to the step change in geometry associated with blade roots and platforms). According to Singer’s analysis [25] LMC allows for at least four fold larger crystal radius than radiation cooling.

There are important challenges, however, if LMC process is to become commercial success. Some of the challenges include, thermal shock failure of the ceramic molds and excessive evaporation of the cooling metal in the vacuum environment. The GCC process in contrast does not require a replacement or a significant modification of the existing Bridgman equipment.

Recently, electron beam cold hearth remelting (EBCHR) has been applied to investment casting of superalloy blades by Howmet [25]. This process has been termed EB casting. In this process, feedstock material is initially melted by an electron beam gun in a vacuum casting furnace. The melt then travels through a water-cooled copper hearth where low-density inclusions such as oxides and nitrides are allowed to rise to the surface where they are trapped (either by the beam or physically restrained by a mechanical dam). Oxygen and nitrogen gas contents are also reduced to equilibrium levels in the vacuum environment.
Once the metal is cleaned, the copper hearth is tilted and the metal is poured into the casting mold. The benefits of EB casting include improved production yields and mechanical properties. There is also the possibility to use revert rather than virgin material which can reduce alloy cost significantly. A potential problem in EB casting is the loss of volatile elements such as chromium. Another drawback is the cost of installation and operation of the additional equipment.

In addition to the LMC, GCC and EB casting processes, Lamilloy single crystal casting [25] and Transient Liquid Phase Bonding technology [26] are used to produce SX turbine blades with very complicate internal cooling channels.

Because the conventional Bridgman process is still the main technology used to cast SX components in the industry, the review of the literature presented below mainly focuses on it.

2.3.2 The Development of Undercooling During the Casting of Single Crystal Turbine Blades/Vanes

The term undercooling refers to the magnitude of the temperature below the equilibrium liquidus temperature. The basic theory of heterogeneous nucleation hinges on the concept of a critical undercooling for nucleation, $\Delta T_N$, needed to overcome the increase in energy associated with surface area creation [27, 28]. Therefore, to begin, it is necessary to understand how regions in SX castings become undercooled during casting in order to then move toward a mechanistic understanding of the formation of spurious grains.
2.3.2.1 Undercooling at the Extremities of a SX Blade/Vane

Single crystal components are cast in large moulds, for example, of usually more than 20 parts for aero-components [29]. Consequently, temperature gradients are lowered and heat flux becomes asymmetric in the conventional Bridgman process resulting in a curved liquidus isotherm. In most industrial conditions the curvature is concave as shown in (Figure 2-3) [7, 11, 14, 17, 30, 31, 32, 33]. Undercooled regions of melt are introduced by this concave shaped liquidus isotherm in those regions where there is a step change in the cross-section of the component - e.g. transition from the blade to the outer shroud. When the curvature is concave, the temperature in the platform edge falls below the liquidus, as the secondary dendrite arms grow outward to fill this region. Meyer ter Vehn et al [14] have measured undercoolings of between 10 and 12K in this region with standard casting parameters. Goldschmidt et al [29] measured a maximum undercooling of 27K for SX castings of CMSX-6 at the withdrawal rates ranging from $1.67 \times 10^{-5}$ to $1.67 \times 10^{-4}$ ms$^{-1}$ (1 to 10 mm/min). In another study [14], experiments revealed high undercoolings of up to 40K in the outer regions of the shroud for large dummy blade cast in SC16 at withdrawal rate of $5 \times 10^{-5}$ ms$^{-1}$ (3 mm/min).

Heterogeneous nucleation can occur in this region if the critical undercooling for nucleation is exceeded before the dendrites arrive. The curvature of the liquidus isotherm in the transition area depends strongly on withdrawal rate as well as on the geometry of blade (both in terms of impact on transverse conduction and on radiative exchange between the heater and/or the baffle). The accumulation of mould ceramic in the transition region also influences heat transfer [29]. Raising the withdrawal velocity causes an increase in the
Various researchers [11, 14, 17] have tried to investigate and hence to reduce the propensity to form undercooled liquid in the blade geometry transition area using a combination of numerical simulation and thermocouple measurements. However, the reduction in the undercooling region by modification of thermal field has proved very difficult practically. For example, isotherm shapes (convex), which are unfavorable for spurious formation, may promote the formation of other defects such as porosity [29, 34].

2.3.2.2 Undercooling of the Dendrite Tip in the Body of a Blade/Vane

The total undercooling observed by a solid dendrite growing in a liquid may be expressed as the sum of the solutal undercooling, $\Delta T_c$, the thermal undercooling, $\Delta T_t$, the curvature undercooling, $\Delta T_r$, and the kinetic undercooling, $\Delta T_k$ and is given by Equation 2-1 [35].

$$\Delta T = \Delta T_c + \Delta T_t + \Delta T_r + \Delta T_k$$

(eq. 2-1)

in the case of conventional castings, the undercoolings associated with thermal diffusion, attachment kinetics, and curvature are small [35] and can be ignored. Thus, the total undercooling may be set approximately equal to the solutal undercooling as in Equation 2-2.

$$\Delta T = \Delta T_c$$

(eq. 2-2)

A number of approaches exist in the literature to calculate the solutal undercooling. Kraft et al. [36] have recently critically reviewed and tested several approaches and concluded
that the Kurz, Giovanola and Trivedi (KGT) [37] model was adequate. Other researchers have also used the KGT model as the basis for estimating dendrite tip growth kinetics in their superalloy solidification models [7, 10, 13, 16, 18, 20, 33].

In the KGT model, the driving force for solute diffusion is the solute build-up at the S/L interface, which can be expressed in terms of the supersaturation $\Omega$ [37]:

$$\Omega = \frac{(C_s^* - C_0)}{(C_l^* - C_s^*)} \quad (eq. \ 2-3)$$

where $C_s^*$ and $C_l^*$ are the solute concentrations at the interface in the solid and in the liquid respectively, and $C_0$ the solute concentration far from the interface. The stationary solute diffusion field around a parabolic dendrite tip has been calculated by Ivantsov [38]. Assuming a paraboloid of revolution to approximate the real dendrite tip shape, the supersaturation $\Omega$ is given as a function of the solutal Péclet number $P_c$:

$$\Omega = I(P_c) = P_c \cdot \exp(P_c) \cdot E_i(P_c) \quad (eq. \ 2-4)$$

$$P_c = \frac{V \cdot \rho}{2 \cdot D^l} \quad (eq. \ 2-5)$$

where, $I(P_c)$ is the Ivantsov function of $P_c$; $V$ (m/s) is the rate of advance of the dendrite tip; $\rho$ (m) is the radius of the dendrite tip; and, $D^l$ (m$^2$/s) liquid diffusion coefficient, $E_i(P_c)$ is the exponential integral function of $P_c$. The Ivantsov function can be written as a continued fraction [35] of the form of Equation 2-6:
Truncating the continued fraction at the second term leads to the following approximations:

\[
I(P_e) = \frac{P_e}{P_e + \frac{1}{1 + \frac{P_e + \frac{2}{1 + \frac{2}{P_e + \ldots}}}}}
\]

(eq. 2-6)

\[
I(P_e) \approx \frac{2P_e}{2P_e + 1}
\]

(eq. 2-7)

The analysis does not permit a unique solution to Equation 2-4 given the available thermal growth conditions. In order to specify a unique solution, Zener [39] proposed the "extremum" theory in which the dendrite tip grows at the maximum velocity for a given supercooling. However, the theory was in poor agreement with the experiments of Glicksman et al. [40]. Much better agreement was found with "marginal stability" theory of Langer and Muller-Krubhaar [41] in which the dendrite grows with a tip radius corresponding to the smallest sinusoidal wavelength \( \lambda_s \), which constitutes an unstable perturbation on a planar solid/liquid interface. The perturbation analysis of Mullins and Sekerka [42] gives:

\[
\lambda_s = \rho = 2\pi \sqrt{\frac{\Gamma \cdot D'}{V \cdot k \cdot \Delta T_0}} = 2\pi \sqrt{\frac{\Gamma}{m \cdot \delta \cdot G_c - G}}
\]

(eq. 2-8)

where, \( \Gamma \) is the Gibbs-Thomson Coefficient (Km), \( G_c \) is the gradient of solute at the solid/liquid interface (wt%/cm) and \( \Delta T_0 \) is the equilibrium solidification interval at the composition \( C_0 \).
In the dendritic growth regime, the effect of the thermal gradient $G$ can be neglected, and for small Péclet numbers $\xi$ is approximately unity [43], thus Equation 2-8 simplifies to:

$$\rho = 2\pi \sqrt{\frac{\Gamma}{m \cdot G_c}} \quad (eq. \ 2-9)$$

Kurz, Giovanola and Trivedi [37] evaluated the solute gradient at the dendrite tip using a flux balance from Ivantsov’s solution:

$$G_e = \frac{V \cdot C_i^* \cdot (k-1)}{D^l} \quad (eq. \ 2-10)$$

An iterative approach is used to determine the solute concentration in the liquid at the tip $C_i^*$. Initially $C_i^*$ is set equal to $C_0$. The Péclet number and supersaturation can then be calculated using Equations 2-10, 2-9, 2-5 and 2-7 and the expression for the supersaturation $\Omega$ (Equation 2-3) can be used to give an improved approximation to $C_i^*$ as follows:

$$C_i^* = \frac{C_0}{1 - (1-k) \cdot I(P_e)} \quad (eq. \ 2-11)$$

Iteration is suspended when the value of $C_i^*$ becomes the same or very close to the value calculated from the previous iteration. The undercooling of the tip is then evaluated from Equation 2-12 for a specified growth rate $V$:

$$\Delta T_c = m \cdot (C_0 - C_i^*) = m \cdot C_0 \cdot \left(1 - \frac{1}{1 - (1-k) \cdot I(P_e)}\right) \quad (eq. \ 2-12)$$

This process is typically used to populate a table of $\Delta T_c$ values for various solidification rates, $V$, for a specific alloy. This dependence can then be approximated using a simple polynomial.
relationship allowing ease of incorporation into microstructure models [20, 33, 44].

The theory presented so far is valid only for binary alloys. An extension to multicomponent alloys may be made by superimposing the solute diffusion fields of each element, $i$, at the dendrite tip. The total undercooling of a multicomponent alloy can then be written as [45, 46]:

$$\Delta T = \Omega \cdot \sum_i m_i \cdot C_{i,i}^* \cdot (1 - k_i) = \Omega \cdot \bar{m} \cdot \bar{C} \cdot (1 - \bar{k})$$  \hspace{1cm} (eq. 2-13)

where the pseudo-binary values $\bar{C}$, $\bar{m}$, $\bar{k}$ are defined as:

$$\bar{C} = \sum_i C_{i,i}^* \hspace{1cm} \bar{m} = \frac{\sum_i m_i \cdot C_{i,i}^*}{\bar{C}} \hspace{1cm} \bar{k} = \frac{\sum_i m_i \cdot C_{i,i}^* \cdot k_i}{\bar{m} \cdot \bar{C}}$$  \hspace{1cm} (eq. 2-14)

In this technique, the concentrations in the liquid $C_{i,i}^*$ are approximated by the average concentrations $C_{0,i}$. The values for the slope of the liquidus, $m_i$, and the partition coefficients, $k_i$ are generally very approximate, as linearized binary Ni-$i$ phase diagrams are typically used. Furthermore, many authors use very different $m_i$ and $k_i$ values for the same alloying element due to the different reference sources, as can be seen in Table 2-5 and Table 2-6 (note the data of ref. [7, 33, 43, 47] were taken from binary phase diagrams). Boettinger et al. [48] calculated the slope of the liquidus, $m_i$, and the partition coefficients, $k_i$ for alloy IN718 using a multicomponent thermodynamic method, a preliminary data base for ten component superalloys consisting of binary coefficients was employed and the extrapolation procedure for higher order systems was used, thus important interactions between the alloying additions were included. The partition coefficients, $k_i$, were compared with experimental measurement
results of Auburtin et al [49] and agreed very well. The data from ref. [48] was also tested by Rappaz et al [50] and were found to be acceptable.

Additional data required for the calculation of dendrite tip undercooling are the diffusion coefficient of solute elements in the liquid \( D^l \) and the Gibbs-Thompson coefficient \( \Gamma \). Cockcroft et al [7] and Fernihough [47] used \( 3.6 \times 10^{-9} \, \text{m}^2\text{s}^{-1} \) and \( 2 \times 10^{-3} \, \text{Km}^{-1} \) as the \( D^l \) and \( \Gamma \) values of Ni base superalloys. Other authors [33, 43, 50] used data very close to these values.

2.4 Heterogeneous Nucleation Kinetics and Spurious Grain Formation Criteria

The nucleation of spurious grains during the directional solidification of single crystal castings is held to be related to the columnar-to-equiaxed transition (CET) in so-far-as both phenomena are related to the kinetics of heterogeneous nucleation and dendrite growth. Various CET mechanisms were proposed, involving broken dendrite arms [7, 12] or freckle chains [21] which acted as nucleating sites for the equiaxed grains, and/or heterogeneous nucleation of equiaxed grains ahead of the columnar interface [21, 9]. It is the latter mechanism that is the most relevant to spurious grain formation in SX castings and hence worthy of further investigation.

2.4.1 Nucleation Kinetics

The rate of nucleation per unit volume in liquid metals has been given by Chalmers [27] as
where

\[ n = \text{the number of atoms per unit volume of liquid;} \]
\[ h = \text{Planck’s constant;} \]
\[ k = \text{Bolzman’s constant;} \]
\[ G_A = \text{free energy change of solidification;} \]
\[ \sigma_{SL} = \text{solid/liquid interfacial surface energy;} \]
\[ L = \text{free energy of vaporization;} \]
\[ T_E = \text{equilibrium melting point of the pure solid;} \]
\[ T = \text{temperature;} \]
\[ \Delta T = \text{supercooling below } T_E. \]

Equation 2-15, predicts that the nucleation rate increases rapidly as the undercooling passes a value defined as the critical undercooling for nucleation. In principle, there are two mechanisms by which a solid may nucleate from a liquid – homogenously (without the aid of a solid substrate) or heterogeneously (with the aid of a substrate). In the case of industrial casting of nickel-based superalloys, it is safe to assume that heterogeneous nucleation is responsible for the spurious grains, as homogeneous nucleation in Ni requires several hundred degrees undercooling [51].

The presence of a foreign substrate changes the free energy balance, reducing the undercooling necessary for nucleation to only a few degrees or less depending on the substrate. The free energy reduction factor \( f(\theta) \) for a spherical capped solid nucleating on a flat substrate may be estimated using Equation 2-16 [51]:
\[ f(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \]  
*(eq. 2-16)*

where \( \theta \) is the wetting angle which the critical solid nucleus makes with the foreign substrate. The resulting changes can reduce the supercooling of nucleation to a fraction of a degree C. Since the value for \( \theta \) is extremely difficult to determine experimentally, the literature on heterogeneous nucleation includes numerous works which attempt to correlate the nucleation substrate, solidifying materials and undercooling of nucleation using simpler mechanisms such as lattice mismatch or electrostatic potential. Experiments with liquid iron, similar in melting point to Ni, have shown that at these temperatures (1823K) the Turnbull-Vonnegut lattice disregistry theory [51] is a good predictor of the undercooling necessary for heterogeneous nucleation. The Turnbull-Vonnegut theory links the lattice mismatch between the foreign substrate and newly forming solid of similar crystallographic structure to nucleation undercooling by:

\[ \Delta T_H = 0.556 \frac{\delta^2}{8} \]  
*(eq. 2-17)*

where, \( \Delta T_H \) is the nucleation undercooling (K) and \( \delta \) is the percent lattice mismatch between substrate and nucleated solid.

Equation 2-17 is based on a simple elastic strain model which is valid up to approximately 20% disregistry. Bramfitt [52] modified the equation to include dissimilar crystal structures evaluated for their planar disregistry in inter-atomic spacings. Bramfitt [52] and Ohashi et al. [53] measured the undercoolings before nucleation on a number of nitrides, carbides and oxides in Fe. Findings were in agreement with Bramfitts version of Turn-
Vonnegut equation and are shown in Figure 2-4 (copied from ref. [47]).

One of the limitations of the classical heterogeneous nucleation (Equation 2-16) is that it assumes that the solid nuclei form as a spherical cap on the substrate. When the wetting angle $\theta$ is less than $\sim 20^\circ$ the spherical cap formed on the substrate is only a few atoms thick and when $\theta$ is less than $\sim 10^\circ$ it falls below a monolayer. Under these conditions, it is unreasonable to assume that the solid nuclei are spherical cap shaped. Consequently, this approach cannot account for the formation of a nucleus at low undercooling unless non-physical surface energies are used [54]. To correct for this, an alternative adsorption model has been proposed [55]. In this model, it is assumed that heterogeneous nucleation takes place by adsorption of the solidifying atoms at the substrate-liquid interface. This model can be used to predict nucleation undercoolings directly from simple phase diagram data for an A-B eutectic or monotectic alloy system. The model has been shown to give good agreement with measurements in the Ag-Pb and Al-Sn alloy system [55]. Although it is impossible to quantitatively apply the adsorption model to complex alloy systems, such as nickel based superalloys, it has potentially provided a better understanding of the heterogeneous nucleation in these systems.

Because of the complex nucleation phenomena in real alloys, a more pragmatic approach to nucleation modeling has been developed by Rappaz [56]. Using statistical arguments, it is assumed that the quasi-instantaneous nucleation behaviour occurs at a family of nucleation sites which is characterized by a continuous (e.g. Gaussian) rather than a discrete distribution, $dn/d(\Delta T)$ (see Figure 2-5). The resulting density of grains at a given
undercooling is given by

\[ n(\Delta T) = \frac{n_{\text{max}}}{\sqrt{2\pi \cdot \Delta T_\sigma}} \exp \left[ -\frac{1}{2} \left( \frac{\Delta T - \Delta T_\sigma}{\Delta T_\sigma} \right)^2 \right] d(\Delta T) \]  

(eq. 2-18)

The parameters of the distribution, \( \Delta T \) (the centre), \( \Delta T_\sigma \) (the standard deviation) and \( n_{\text{max}} \) (the total number of nucleation sites available) must be evaluated experimentally for the particular alloy. A second, separate, distribution may exist for the mould face coat, which would also require characterization. The appeal of this model is that the nucleation rate is always finite even at small undercoolings [7], thus it is well suited for the investigation of spurious grains.

### 2.4.2 Criteria for CET

A popular view in the investment casting literature concerning the CET in superalloys is that it occurs at a critical value of \( G/V \), although no experiment has ever validated this theory. McLean's [57] well-known plot of the solid/liquid interfacial morphology as a function of \( G \) and \( V \) for common industrial superalloys is an excellent example of this. Moreover, the aerospace investment casting industry often publishes "defect maps" [58] based on graphs of \( G \) and \( V \) similar to McLean's, in which the probability of equiaxed grain formation is shown to increase as \( G/V \) decreases.

In another approach, Pollock et al. [12] studied the formation of spurious grain promoted by thermosolutal convection and suggested a thermosolutal convection criterion for the CET phenomena in superalloy single crystal castings. However, inclusions as
heterogeneous nucleants were not considered in their study.

Many CET criteria [37, 59, 60, 61, 62, 63, 64] have been suggested for binary alloys, among these, that of Hunt's [59, 64] for Al-3wt%Cu alloy has been most extensively used by modelers. It considers heterogeneous nucleation in the constitutionally undercooled liquid ahead of the growing columnar front to be the only source for equiaxed grains. Hunt assumed that the microstructure would be fully equiaxed when the volume fraction of equiaxed grains exceeded 0.49 and that the microstructure would be fully columnar when the volume fraction of equiaxed grains was less than 0.0049. Hunt went on to develop the following criteria for equiaxed and for fully columnar, respectively

\[
G < 0.617N_0^{1/3} \left[ 1 - \frac{\Delta T_N}{(\Delta T_C)^3} \right] \Delta T_C \quad \text{Equiaxed} \quad (eq. 2-19)
\]

\[
G > 2.86N_0^{1/3} \left[ 1 - \frac{\Delta T_N}{(\Delta T_C)^3} \right] \Delta T_C \quad \text{Columnar} \quad (eq. 2-20)
\]

where

\[ G = \text{thermal gradient at the liquid/solid interface (K/m)}; \]
\[ N_0 = \text{nucleation site density (m}^{-3}\text{)}; \]
\[ \Delta T_C = \text{columnar dendrite tip undercooling (K)}; \]
\[ \Delta T_N = \text{heterogeneous nucleation undercooling at which one site per cc per second becomes active (K)}. \]

The Hunt model assumes a constant thermal gradient in the liquid ahead of the columnar front and that heterogeneous nucleation in the constitutionally undercooled region at
The solidification characteristics of IN718 has been investigated by C.A. Matlock et al [65] using experiments in which samples were directionally solidified in a conventional Bridgman furnace utilizing a variety of solidification rates and thermal gradients shown in Table 2-7. It was found that as the solidification rate is increased, the axial progression of the columnar growth front is blocked by radial growth of equiaxed grains, and the equiaxed morphology becomes increasingly preferred. The columnar-to-equiaxed transition does not occur at a discrete velocity but happens over a range of velocities from $2.5 \times 10^4$ to $7.5 \times 10^4$ ms$^{-1}$ (15.0 to 45.0 mm/min). Hunt’s theory and a simplified velocity-undercooling relationship were used to calculate the critical thermal gradients assuming that $\Delta T_n = 0.75 ^\circ C$, $N_0 = 1000/cm^3$, the theoretical boundaries for the columnar-to-equiaxed transition zone together with the experimental results of Matlock et al [65] are presented in the solidification map of Figure 2-6. The experimentally observed microstructures correlated well with the theoretical prediction of the boundaries of the transition zone.

2.4.3 Criteria for the Formation of Spurious Grains in the Shroud/Platform Corner of a Blade/Vane

The solidification conditions prevailing when a columnar dendritic front passes an enlargement in the cross-section of the component (Figure 2-7(a)) was studied in detail by Cockcroft et al. [7]. A criterion was proposed based on the ability of a secondary arm to traverse the platform length, $d_p$, prior to the undercooling at the tip, $T_s$, exceeding the critical
undercooling for heterogeneous nucleation, $\Delta T_{\text{nuc}}$ - e.g.

$$\Delta T_s \geq \Delta T_{\text{nuc}} @ d_s = d_p \quad \text{spurious grain} \quad \text{(eq. 2-21)}$$

$$\Delta T_s \leq \Delta T_{\text{nuc}} @ d_s = d_p \quad \text{no spurious grain} \quad \text{(eq. 2-22)}$$

where $d_s$ is the distance traveled by the secondary arm.

$$\Delta T_s = V \cdot G \cdot t + \Psi(d_s) \quad \text{(eq. 2-23)}$$

where $V$ is mould withdrawal velocity, $G$ is the axial temperature gradient, $t$ is time and $\Psi$ is some function describing the transverse variation in temperature with distance. The distance traveled by the secondary arm

$$d_s(t) = \int_0^t V_s dt \quad \text{(eq. 2-24)}$$

where $V_s$ is the growth velocity of the secondary dendrite and is determined using the KGT model as described above. Equation 2-22 is solved numerically using a time-stepping technique, in which $\Delta T_{\text{nuc}}$ was measured experimentally.

A. de Bussac and Ch.-A. Gandin [15] have developed the criteria for the formation of stray crystals at platform ends under the conditions shown in Figure 2-7(b) and (c) for the converging dendrites (Figure 2-7(b)) and for diverging dendrites respectively, as well as a criterion for the formation of spurious grain ahead of the steady columnar front. However, due to their complicated mathematic form, these criteria will not be introduced here.
2.5 Inoculation Theory for Casting Process and the Parameters Controlling the Growth of EQ Grains in the Inoculation Process

Because the present research is focused on the nucleation of spurious grains on the base of inclusions present in the melt; it is of interest to review the inoculation theory for casting processes. Inoculation via introduction of extraneous particles has been used as a grain refinement method for superalloy castings for a long time [66, 67, 68, 69, 70]. Those reported to act as effective inoculants in various superalloys includes oxides such as CoO, NiO, Al₂O₃ and others [66, 67], boron [69] and borides such as ZrB₂, TiB₂ [67], carbides like TiC [67], ZrC, NbC [69], and intermetallic compounds like NiAl, Ni₂Al₃ [69] and NiₓAlᵧTi₂[70]. However, the potency of these inoculants is different for different alloys, for example, while carbides were found an effective inoculants for Ni-2%Cr-2.5%Mn alloy [68] and IN738LC [69], they were reported to have no effect on nucleation in the castings of alloy IN718 [71].

The final grain size in an alloy depends on a combination of the local nucleation kinetics, growth kinetics and the rate of heat extraction. The nucleation kinetics establish, or determine, the number of nuclei that form at a given undercooling. Once nucleated, the grains begin to grow at a rate dependent on the local undercooling and release latent heat. The balance between the rate of heat release and the rate of heat extraction determines the local thermal history (extent to which thermal recalescence occurs if any), which in turn dictates the local peak undercooling and number of active nuclei, for a given alloy composition, and ultimately the as cast grain size.
In early work [72], the degree of growth restriction for a particular solute was described by the constitutional-supercooling parameter $P$

$$P = \frac{m(k-1)C_0}{k}$$  \hspace{1cm} (eq. 2-25)

where $m$ is the liquidus slope, $k$ is the equilibrium partition coefficient, and $C_0$ is the solute content. As reviewed by Greer et al [73], in the absence of solute interactions, the overall constitutional-supercooling parameter for a multicomponent alloy can be estimated by summing the $P$ values for each element.

Maxwell and Hellawell [74] consider the growth of spherical crystals restricted by the partitioning of a single solute. To a good approximation the crystal growth rate for a given undercooling is proportional to the diffusivity of the solute in the liquid and inversely proportional to the parameter $Q$ which is termed the growth-restriction parameter.

$$Q = m(k-1)C_0 = kP$$  \hspace{1cm} (eq. 2-26)

The $Q$ parameter can also be extended to multicomponent alloys with the simple additive sum of the $Q$ values for the individual solutes.

Studies [73, 75] showed that there appears to be a universal curve relating grain size to $P$. As $P$ is increased, the grain size at first decreases sharply, and then levels off at higher values. The study of Greer et al [73] found that the experimental data could be better interpreted in terms of $Q$. In any event, a relatively concentrated alloy (high values of
growth-restriction parameter $P$ or $Q$) will necessarily have a slower growth rate for a given undercooling. As a result, larger maximum undercoolings are achieved and a higher grain density (finer grain size) is obtained.

2.6 Nitrides as Heterogeneous Nucleation Sites of Spurious Grains

Spurious grains have been found in many single crystal superalloy castings in the absence of any freckling or drastic change in the thermal conditions – see for example Figure 2-8. One possibility is the nucleation on non-metallic inclusions like nitrides and/or oxides.

The role of titanium as a nucleant in cast steels has been known for some time [52, 76, 77, 78, 79, 80]. Pardo [81] found the CET to occur in ferritic stainless steel GTA welds only in the presence of TiN particles. Bramfitt [52] also found it to be effective nucleating agent at an undercooling of 1.7°C. Inclusions were observed by Villafuerte et al. [82] at the origin of equiaxed ferritic dendrites in the grain refined welds. The studies by Poole et al. [83] have revealed that TiN is an effective nucleant for ferritic stainless steels, which have been directionally solidified slowly, but is not an effective inoculant for austenitic stainless steels. The distinction arises because, the lattice mismatch (2.9315 Å) between TiN, which has a NaCl crystal structure, and ferritic matrix is less when compared to the lattice mismatch between TiN and the austenitic matrix (3.6773 Å). Hence, TiN is able to induce heterogeneous nucleation in ferritic stainless steel.
Investigations of superalloys using the EB button melting technique have showed the presence of oxides and nitrides [84] and also the presence of TiN in high temperatures in liquid superalloys [85, 86, 87]. Studies on revert alloys have attributed the presence of equiaxed grains on high [N] levels [88].

C. A. Carney et al. [9] found that slivers in single crystal turbine blades were often associated with oxide inclusions. D. A. Ford et al. [21] found that nitrogen could be the strongest agent in promoting spurious grains. The probable source of nitrogen was identified as originating from the outgassing of the investment mould when cast under vacuum. After pouring the desorption of nitrogen is followed by the formation of titanium nitride compounds which can block dendrite growth, or which act as substrates for crystal growth. Valuable crystallographic data have been provided in their paper. The authors also ranked the order of some inclusions as potential nucleants. However, direct evidence of nitrides as nuclei of spurious grains in SX superalloy casting is still needed.

2.7 The Competitive Growth of Spurious Grains

The competitive growth of a seeded crystal and the spurious grains formed at the mould/seed gap during directional solidification has been investigated by D'Souza et al [89]. The S/L interface curvatures were found to be an important factor influencing the competitive growth of grains with different orientations. With a curved S/L interface, the stability of grains was explained by relating the grain orientations to the local normals to S/L interface, through the angle $\angle^G_{\text{<001>}}$, which defines the deviation of <001> growth direction from the
local normal to the solid-liquid interface. The stable growth of grains was found to correlate with a relatively low value of $\angle_{<001}>$. In the case of planar isotherms, the thermal gradient is uniaxial and normal to the ingot cross section and the angle $\angle_{<001>}$ is identical to the deviation of $<001>$ direction from the vertical macroscopic axis. It follows therefore that an exact $<001>$ axial texture is to be expected in the case of planar liquidus isotherms, as in the classical grain selection process [90]. However, as indicated previously, in the industrial SX casting processes curved rather than planer liquidus isotherms are found. There will be a range of orientations that are locally stable. A grain with a larger $\angle_{<001>}$ would be overgrown despite it having a near $<001>$ axial orientation, and a spurious grain will persist with $<001>$ far from the macroscopic growth axis but with a similar or lower $\angle_{<001>}$ than for the SX matrix. The same authors also proposed that minor differences in alloy composition significantly alter the interdendritic liquid composition, which reduces the efficiency of secondary and tertiary dendrite development in CMSX4, allowing edge-stabilized grains to extend throughout the casting.

2.8 Thermal Chemistry of Nitride Inclusion

In order to understand the influence of nitride particles on the heterogeneous nucleation in an undercooled liquid, the thermal chemistry of this inclusion has to be studied. Non-metallic inclusions in superalloys may generally be classified into two categories: indigenous, precipitated during solidification, and exogenous, present in the liquid before solidification. The precipitation of inclusions during solidification is controlled by the
appropriate solubility limit. As the solidification proceeds, constitutional interdendritic segregation will cause inclusions such as Al₂O₃ and nitrides.

2.8.1 The Saturation Solubility of TiN in Fe-Cr-Ti-Ni System

The solubility of nitrogen in iron, iron-nickel alloys [91, 92] and in multicomponent nickel-based alloys [93] has been reported in the literature. On the basis of statistical theory for the lattice model of solutions, Bol'shov et al. [93] derived a formula for the solubility of nitrogen in alloys of iron and hypothetically, nickel with transition metals in the form

\[
[\%N] = [\%N]_{Me} \frac{A_{Me}}{A_{M}} \left(1 - \frac{1}{6} \sum_{j=3}^{n} c_{Nj} x_j \right)^6
\]

(\text{eq. 2-27})

where, \( [\%N] \) and \( [\%N]_{Me} \), are the solubility of nitrogen (in mass fractions) at \( P_{N_2} = 1 \text{ atm} \), and the temperature 1600 °C in an alloy \( M \), and in a pure metallic solvent \( Me \), respectively. \( x_j \) is the mole fraction of the \( j \)-th component in the alloy; \( c_{Nj} \) is the Wagner interaction parameter of nitrogen with the \( j \)-th component in the solvent \( Me \); \( n \) is the number of components in the alloy; and \( A_{M} = A_{Me} x_{Me} + \sum A_j x_j \), where \( A_j \) is the atomic mass of the \( j \)-th component.

Studies have shown that Sievert's law holds for molten, pure iron over modest nitrogen pressures and for all titanium bearing alloys up to a nitrogen partial pressure below 1 atm. [86, 94]. The dissolution of nitrogen in liquid iron alloy can be written as:

\[
\frac{1}{2} N_2 (g) = [N]_{(\text{wt}\%)}
\]

(\text{eq. 2-28})
where, $K$ is the equilibrium constant for the reaction and $f_N$ is the activity coefficient of nitrogen relative to a 1 wt% standard state in iron. The activity coefficient of nitrogen can be calculated using the known thermodynamics:

$$\log f_N = \sum_i e_i^N [\%i] \quad (eq. 2-30)$$

where, $e_i^N$ is the first order interaction coefficient between nitrogen and element $i$. The standard free energy of solution of nitrogen is given by:

$$\Delta G^o = \Delta H - T \Delta S^o = -RT \ln K \quad (eq. 2-31)$$

where $\Delta H^o$ and $\Delta S^o$ represent the standard enthalpy and entropy of nitrogen solution at temperature $T$. Using the above relations, the solubility of nitrogen in various iron-based alloys can be calculated.

As pointed out by Mitchell [97], the reaction between Ti and N is determined for alloys that contain over 0.2 wt% Ti.

$$TiN (s) = [Ti] + [N] \quad (eq. 2-32)$$

The Gibbs Standard free energy for the above reaction is given by:

$$\Delta G^o = -RT \ln(K_{sp}) \quad (eq. 2-33)$$

where $K_{sp}$, is the solubility product of TiN in a superalloy which is defined as:
\[ K_{sp} = [Ti \text{ wt\%} \times f_{Ti}] \times [N \text{ wt\%} \times f_{N}] \]  

(eq. 2-34)

where, \( f_i \) is the activity coefficient of component \( i \). The activity coefficient of Ti is given by the expression:

\[
\log f_{Ti} = \sum e'_{Ti}[\%i] 
\]

(eq. 2-35)

where \( e'_{Ti} \) is the first order coefficient of Ti and the element \( i \).

Equation 2-32 is temperature controlled such that the equilibrium shifts to the right with increasing temperature. It is also composition dependent, being controlled by the activity coefficients and contents of Ti and N, and hence being a function of segregation during freezing.

2.8.2 The Saturation Solubility of TiN in Alloy IN718 and SX Alloys with High Ti Content

The solubility of N in nickel-based alloy IN718 by equilibration methods has been extensively studied [95, 96, 97, 98, 99]. The solubility of nitrogen increases with increasing temperature. An increase in nitrogen content in the liquid alloy can result in the precipitation of TiN particles at the liquidus temperature in alloys like IN718, which have low titanium levels. In addition, the nitrogen content in the alloy was found to affect the size of TiN particles as shown in Figure 2-9 [97].

It has been shown that the saturation solubility of TiN is not only a function of the Ti
and N content, but can also be affected by Cr content. The solubility of TiN is found to increase with Cr content [86, 92, 97]. The solubility of N in IN718 at 1613K, as determined from the solubility product of TiN, was reported [85] as approximately 39ppm N, which implies that in the typical wrought commercial alloy at 60 ppm N, approximately 1/3 of the total N content will be present at that temperature as solid TiN particles in the liquid. Experimental work indicates that most of the remainder is precipitated between the liquidus and solidus, however, as reported by Sandararajan [85], TiN particles precipitated in the solid/liquid mushy zone will not float out of the interface, they therefore have little influence on the nucleation of new grains. Cockcroft et al [99] found that approximately 1 ppm N is still in solution at the end of freezing and available for precipitation in the solid state. The same authors [99] have also reported the saturation solubility relationships for TiN as a function of temperature and partial pressure of nitrogen \( (P_{N_2}) \) in alloy IN718 as given in Table 2-8. It can be seen that TiN is highly stable at these process temperatures (1700 K) and under high vacuum. In the case of single crystal alloys, due to the higher titanium content the solubility of titanium nitride is lower in these alloys.

2.9 Summary of Literature Review

The SX alloys and SX blade casting processes have been briefly reviewed in this chapter. Special attention has been given to the new casting techniques and SX alloys applied or developed for IGT SX castings. Among the main challenges in the scale-up from small aero-engine SX castings to large IGT SX castings are the larger cross-section area change and more severe S/L interface curvature. Consequently undercooled regions may exist in the
blade, which makes the IGT SX components more vulnerable to the attack of solidification defects such as spurious grains. Various models, especially the KGT model, for the calculation of undercooling in a solidification front were critically reviewed. Nitrogen content has been reported to have influence on the nucleation of spurious grains in superalloys. Nitride inclusions such as TiN particles were then hypothesized as one of the main causes of spurious grain nucleation, however no direct evidence was found. Heterogeneous nucleation kinetics and the various criteria for predicting the columnar to equiaxed (CET) transition solidification were discussed. The CET in alloy IN718 was found to have been extensively investigated. Attention has also been given to the investigations about competitive growth between grains with different crystallographic orientations. It was also found that the inoculation practice used in the industry provided theoretical tools to compare the tendency of different alloys to nucleate equiaxed grains on the same nucleants. Finally, the thermochemistry of nitrides was reviewed to understand the behavior of nitrogen and nitrides in the superalloy liquid melt, specially for alloy IN718.
Table 2-1. Nominal composition of Some First Generation Single Crystal Superalloys wt.%.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>V</th>
<th>Cb (Nb)</th>
<th>Al</th>
<th>Ti</th>
<th>Hf</th>
<th>Ni</th>
<th>Density</th>
<th>Ref</th>
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<td>5</td>
<td>-</td>
<td>4</td>
<td>12</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>6</td>
<td>4</td>
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<td>-</td>
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<td>4</td>
<td>5.5</td>
<td>-</td>
<td>-</td>
<td>5.8</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.2</td>
<td>[5]</td>
</tr>
<tr>
<td>Nasair 100</td>
<td>9</td>
<td>-</td>
<td>1</td>
<td>10.5</td>
<td>3.3</td>
<td>-</td>
<td>5.75</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.54</td>
<td>[3]</td>
</tr>
<tr>
<td>AF-56 [SX 792]</td>
<td>12</td>
<td>8</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>-</td>
<td>3.4</td>
<td>4.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.25</td>
<td>[2]</td>
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</table>

Table 2-2. Nominal Composition of Some Second Generation Single Crystal Superalloys wt.%.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>Re</th>
<th>Al</th>
<th>Ti</th>
<th>Nb</th>
<th>Hf</th>
<th>Ni</th>
<th>Density</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMSX-4</td>
<td>6.5</td>
<td>9</td>
<td>0.6</td>
<td>6</td>
<td>6.5</td>
<td>3</td>
<td>5.6</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>8.70</td>
<td>[2]</td>
</tr>
<tr>
<td>PAW 1484</td>
<td>5</td>
<td>10</td>
<td>2</td>
<td>6</td>
<td>9</td>
<td>3</td>
<td>5.6</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>8.95</td>
<td>[2]</td>
</tr>
<tr>
<td>SC180</td>
<td>5</td>
<td>10</td>
<td>2</td>
<td>5</td>
<td>8.5</td>
<td>3</td>
<td>5.2</td>
<td>1.0</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>8.84</td>
<td>[2]</td>
</tr>
<tr>
<td>MC2</td>
<td>8</td>
<td>5</td>
<td>2</td>
<td>8</td>
<td>6</td>
<td>-</td>
<td>5.0</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.63</td>
<td>[2]</td>
</tr>
<tr>
<td>SMP14</td>
<td>4.8</td>
<td>8.1</td>
<td>1</td>
<td>7.6</td>
<td>7.2</td>
<td>3.9</td>
<td>5.4</td>
<td>-</td>
<td>1.4</td>
<td>-</td>
<td>9.02</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>DD6</td>
<td>4.3</td>
<td>9</td>
<td>2</td>
<td>8</td>
<td>7.5</td>
<td>2</td>
<td>5.6</td>
<td>-</td>
<td>0.5</td>
<td>0.1</td>
<td>-</td>
<td>8.83</td>
<td>[5]</td>
</tr>
<tr>
<td>René N-5</td>
<td>7</td>
<td>8</td>
<td>2</td>
<td>5</td>
<td>7</td>
<td>3</td>
<td>6.2</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>8.70</td>
<td>[2]</td>
</tr>
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</table>
Table 2-3 Chemical Compositions (Wt.%) of Some Third Generation Ni-Based Superalloys for Single Crystal Blades. [3]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>Re</th>
<th>Al</th>
<th>Ti</th>
<th>Nb</th>
<th>Hf</th>
<th>Others</th>
<th>Ni</th>
<th>Density kg/dm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMSX-10</td>
<td>2</td>
<td>3</td>
<td>0.4</td>
<td>5</td>
<td>8</td>
<td>6</td>
<td>5.7</td>
<td>0.2</td>
<td>0.1</td>
<td>0.03</td>
<td>-</td>
<td>BAL</td>
<td>9.05</td>
</tr>
<tr>
<td>René N6</td>
<td>4.2</td>
<td>12.5</td>
<td>1.4</td>
<td>6</td>
<td>7.2</td>
<td>5.4</td>
<td>5.75</td>
<td>-</td>
<td>-</td>
<td>0.15</td>
<td>0.05C</td>
<td>BAL</td>
<td>8.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.004B</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.01Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy 5A</td>
<td>4.5</td>
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<td>-</td>
<td>5.7</td>
<td>7</td>
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<td>6.25</td>
<td>-</td>
<td>-</td>
<td>0.15</td>
<td>0.05C</td>
<td>BAL</td>
<td>8.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.004B</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.01Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMS-75</td>
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<td>12</td>
<td>2</td>
<td>6</td>
<td>6</td>
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<td>6</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>BAL</td>
<td>-</td>
</tr>
<tr>
<td>TMS-80</td>
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<td>5.8</td>
<td>4.9</td>
<td>5.8</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>3Ir</td>
<td>BAL</td>
<td>-</td>
</tr>
<tr>
<td>MC-NG</td>
<td>Patent pending</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BAL</td>
<td>8.75</td>
</tr>
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Table 2-4 Chemical Compositions of Typical SX Alloys Used in Land Base Turbine Engines.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>Re</th>
<th>Al</th>
<th>Ti</th>
<th>C</th>
<th>Nb</th>
<th>B</th>
<th>Zr</th>
<th>Hf</th>
<th>Ni</th>
<th>Density kg/dm³</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMSX-4</td>
<td>6.5</td>
<td>9</td>
<td>0.6</td>
<td>6</td>
<td>6.5</td>
<td>3</td>
<td>5.6</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>BAL</td>
<td>8.70</td>
</tr>
<tr>
<td>PAW 1483</td>
<td>12.2</td>
<td>9.0</td>
<td>1.9</td>
<td>3.8</td>
<td>5</td>
<td>-</td>
<td>3.6</td>
<td>4.1</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>BAL</td>
<td>-</td>
</tr>
<tr>
<td>SC16</td>
<td>16</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>3.5</td>
<td>-</td>
<td>3.5</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>BAL</td>
<td>8.21</td>
</tr>
<tr>
<td>RR3000</td>
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<td>3.25</td>
<td>0.5</td>
<td>5.5</td>
<td>8.25</td>
<td>6</td>
<td>6</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>BAL</td>
<td>68</td>
</tr>
<tr>
<td>YH61</td>
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<td>1.0</td>
<td>0.9</td>
<td>8.8</td>
<td>8.8</td>
<td>1.4</td>
<td>5.0</td>
<td>-</td>
<td>0.07</td>
<td>0.8</td>
<td>0.02</td>
<td>-</td>
<td>0.25</td>
<td>BAL</td>
<td>-</td>
<td>[101]</td>
</tr>
<tr>
<td>CM 186 LC*</td>
<td>6</td>
<td>9</td>
<td>0.5</td>
<td>8</td>
<td>3</td>
<td>3</td>
<td>5.7</td>
<td>0.7</td>
<td>0.07</td>
<td>-</td>
<td>0.015</td>
<td>0.005</td>
<td>1.4</td>
<td>BAL</td>
<td>8.70</td>
<td>[102]</td>
</tr>
</tbody>
</table>

* This second generation DS superalloy is recently cast as SX vane segments of industry gas turbines with an increased tolerance for grain defects to improve casting yield and reduce component cost [102].
Table 2-5 Partition Coefficients of Alloying Elements in IN718.

<table>
<thead>
<tr>
<th>Elements</th>
<th>$C_i$</th>
<th>$m_i$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>18.12</td>
<td>-1.91</td>
<td>-1.9</td>
<td>-3</td>
<td>-3</td>
</tr>
<tr>
<td>Co</td>
<td>0.2</td>
<td>3.72</td>
<td>-0.4</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Mo</td>
<td>2.96</td>
<td>-5.49</td>
<td>-0.001</td>
<td>-4.8</td>
<td>-4.8</td>
</tr>
<tr>
<td>Nb</td>
<td>5.27</td>
<td>-9.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>0.46</td>
<td>-14.1</td>
<td>-4</td>
<td>-13</td>
<td>-14</td>
</tr>
<tr>
<td>Ti</td>
<td>1.0</td>
<td>-21.1</td>
<td>-11.5</td>
<td>-16</td>
<td>-16</td>
</tr>
<tr>
<td>Fe</td>
<td>18.24</td>
<td>-0.141</td>
<td>-1.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2-6 Liquidus Slopes of Alloying Elements in IN718.

<table>
<thead>
<tr>
<th>Elements</th>
<th>$C_i$</th>
<th>$k_i$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>18.12</td>
<td>1.19</td>
<td>0.6</td>
<td>0.92</td>
<td>1.12</td>
</tr>
<tr>
<td>Co</td>
<td>0.2</td>
<td>1.4</td>
<td>1</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>Mo</td>
<td>2.96</td>
<td>0.78</td>
<td>1</td>
<td>0.57</td>
<td>0.9</td>
</tr>
<tr>
<td>Nb</td>
<td>5.27</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
<td>0.35</td>
</tr>
<tr>
<td>Al</td>
<td>0.46</td>
<td>0.64</td>
<td>0.6</td>
<td>0.83</td>
<td>1.2</td>
</tr>
<tr>
<td>Ti</td>
<td>1.0</td>
<td>0.24</td>
<td>0.5</td>
<td>0.89</td>
<td>0.55</td>
</tr>
<tr>
<td>Fe</td>
<td>18.24</td>
<td>1.16</td>
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<td>-</td>
<td>1.16</td>
</tr>
<tr>
<td>Ni</td>
<td>53.75</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.02</td>
</tr>
</tbody>
</table>
Table 2-7. Solidification Velocity and Thermal Gradients Used in IN718 CET Experiments by Matlock [65].

<table>
<thead>
<tr>
<th>Solidification Velocity (cm/sec)</th>
<th>1375</th>
<th>1380</th>
<th>1400</th>
<th>1500</th>
<th>1600</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>189</td>
</tr>
<tr>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>108</td>
<td>182</td>
</tr>
<tr>
<td>0.010</td>
<td>13*</td>
<td>17*</td>
<td>32*</td>
<td>106</td>
<td>161</td>
</tr>
<tr>
<td>0.025</td>
<td>-</td>
<td>-</td>
<td>34*</td>
<td>106</td>
<td>171</td>
</tr>
<tr>
<td>0.050</td>
<td>-</td>
<td>-</td>
<td>38</td>
<td>146</td>
<td>261</td>
</tr>
<tr>
<td>0.075</td>
<td>-</td>
<td>-</td>
<td>20**</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.100</td>
<td>-</td>
<td>-</td>
<td>23**</td>
<td>53**</td>
<td>83**</td>
</tr>
</tbody>
</table>

*Gradient calculated from a 1-D model and verified by thermocouple data.

**Gradients determined from thermocouple data during equiaxed growth while the 1-D thermal model is not valid.

Table 2-8. Saturation Solubility of TiN in IN718 [99].

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$p_{N_2}$ (atm)</th>
<th>Saturation [N] (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1700</td>
<td>$4.8 \times 10^{-5}$</td>
<td>39</td>
</tr>
<tr>
<td>1800</td>
<td>$4.0 \times 10^{-4}$</td>
<td>112</td>
</tr>
<tr>
<td>1900</td>
<td>$2.7 \times 10^{-3}$</td>
<td>290</td>
</tr>
<tr>
<td>2000</td>
<td>$1.2 \times 10^{-2}$</td>
<td>620</td>
</tr>
</tbody>
</table>
Figure 2-1. Directional solidification process employed to cast single crystals [22].
Figure 2-2. Turbine blade geometry with indication of the typical locations of stray crystals formed during solidification. [12].
Figure 2-3. Depending on the undercooling capacity of the given alloy a macroscopic concave curvature of the liquidus isotherm can cause the formation of spurious grains (a) or result in fast lateral growth of secondary dendrites (b).
Figure 2-4 Lattice misfit vs. nucleation undercooling in Fe of various oxides, nitrides and carbides. (copied from ref. [47]).
Figure 2-5 Continuous distribution of nucleation sites used in modelling of equiaxed solidification [56].
Figure 2-6. Morphologies of directionally solidified IN718 mapped on a plot of the dominant thermal parameters: growth velocity and calculated thermal gradient [65].
Figure 2-7. Schematic of stray crystal formation and dendritic growth of single crystal in the presence of (a) a cross-section enlargement and (b) and (c) internal walls [15].
Figure 2-8. Spurious grain with no obvious source of origin. [21]
Figure 2-9. Size distribution of TiN inclusions as a function of nitrogen content in alloy IN718, with a constant local solidification time [97].
Chapter 3 Objectives

The overall objective of this work is to investigate the effectiveness of TiN inclusion particles as a nucleation agent for the formation of spurious grains during the SX casting process. For the purpose of this study, alloy IN718 has been tested instead of a SX alloy because its thermal-chemistry property data at high temperature are relatively well known.

To accomplish this task the following sub-tasks were completed.

1. Cast SX ingots with a simple geometry shape of alloy IN718 with three different nitrogen contents, which are below, close to and above the saturation nitrogen content for TiN particles. Withdrawal rate of the casting process was varied to reveal the behaviour of TiN particles as a nucleant under different solidification front undercoolings;

2. Develop a thermal model of the casting process by using the commercial software package ABAQUS to calculate the thermal gradient and solidification velocity in each cast ingot, and verify the thermal model with thermocouple measurements;

3. Calculate the undercooling at the solidification front by using the output from the thermal model and the KGT model;

4. Estimate the nucleation kinetics of spurious grains based on TiN particles using Hunt's CET model.
Chapter 4 Experimental Methodology

Cylindrical single crystal samples were cast in a Bridgman furnace at UBC. Due to the small diameter of the ceramic mold for the casting, it was not feasible to attach a pig tail crystal selector at the bottom of the mold. The seed method was therefore chosen in the experiments. The seeds were made in a directional solidification and quench (DSQ) vacuum induction furnace. The withdrawal rates examined in the study were varied to change the undercooling at the liquid/solid interface. All the casting samples were cut along the centerline and macro-etched to examine the grain structure, and photo micrographs were taken. Thermocouples were used in three castings to record the thermal history, which was then used for the validation of the ABAQUS model. The ABAQUS model was used to predict the local solidification conditions present during the casting including in those experiments where thermocouples were not used.

4.1 Choice of Alloys

IN718 was selected for the tests because the nitrogen solubility (39ppm at $T_L = 1613K$ ($1340^\circ C$)) is reasonably well understood [85]. The principal difficulty in previous work has been that the alloys chosen have a very low N solubility and it is therefore hard to guarantee the complete absence of TiN inclusions in a given situation. In the solid/liquid mushy region, due to the combined effect of factors such as: a) varying temperature, b) segregation of Ti and nitrogen, the solubility limit may be reduced to below the bulk limit of 39ppm (i.e. TiN precipitation may occur in the segregation zone).
Experiments [85] have established that TiN particles precipitated in the solid/liquid mushy zone will tend not float out. To ensure an absence of TiN particles, an IN718 alloy with a very low nitrogen content (< 20ppm) was used in the experiments. The composition of normal IN718 alloy and IN718 with very low nitrogen content (IN718PSQ used in UBC) can be found in Table 4-1.

4.2 Alloy Nitrogen Content Control

IN718 was cast in a Bridgman furnace at UBC with three [N] contents: < 20ppm (IN718PSQ), ~ 45ppm (normal IN718) and ~ 100ppm (IN718N). The charge materials for IN718PSQ and normal IN718 were as ordered material from the companies given in Table 4-1. The IN718N charge material was made at UBC before casting. It is well known that CrN particles dissolve at temperatures above the liquidus of IN718 [85], therefore the CrN powder instead of TiN powder can be used to increase the [N] of the charge materials. Pure CrN powder (provided by Special Metal Corp.) was added into a small hole at one end of the IN718 bar with a dimension of 150mm × dia. 20mm, the amount of CrN powder was calculated so that the [N] content of the remelted ingot would be around 100ppm. The IN718 bar was then put into a 22.2mm ID alumina tube crucible with the hole facing up, it was then remelted at the UBC Bridgman furnace under a 133 Pa N₂ pressure. The ingot was refined for 2000 seconds at a maximum temperature of 1773K (1500°C) to have the CrN particles completely dissolved and [N] evenly distributed by convection in the liquid. The casting was then withdrawn from the hot zone of the furnace at a speed of $3.4 \times 10^{-4} \text{ m/s}$ (20.5 mm/min) and cooled down to room temperature. The ingot surface was ground by a belt sander to
remove any ceramic inclusions from the crucible; it was then charged to the ceramic mould with the end originally containing the small hole containing CrN powder facing down. [N] and [O] contents were analyzed for all the IN718N alloy castings at Allvac by fusion analysis on a Leco TC436. The samples used for analysis were cut at UBC by using a water-base coolant cooled SiC wheel blade. Because ingots of IN718 and IN718PSQ were cast from as-ordered material, only 2 samples of the normal IN718 and IN718PSQ alloy castings were analyzed using the same method at Allvac.

4.3 The Design of the Geometric Shape of the Casting

The sample shown in Figure 4-1 was cast for the study. The overall height is ~12 cm. The angle of the conical transition between the single crystal seed and the cylinder was varied from 45° to 75° relative to the end plane of the cylinder. It was found that a single crystal can be most easily cast when the transition angle was 75°. Two cast samples are shown in Figure 4-2. The sample with a 45° transition completely failed to produce single crystal; whereas the one with 75° transition produced a cylinder with only two spurious grains originating from surface defects at the adapter area. It is a common phenomenon that a sudden cross section area change may cause the formation of spurious grains, as mentioned in Chapter 2. The larger and more abrupt the area change, the higher the tendency for spurious grains to appear. The 75° adapter was then used for all the remaining tests conducted during the study.
Single crystal seeds were made using a smaller, so-called directional solidification and quench (DSQ) vacuum induction furnace. A schematic of the furnace is shown in Figure 4-3. The quenching system was not used in making the single crystal seeds and was not introduced here. The main chamber of the DSQ furnace consists of an outer quartz tube and an inner graphite susceptor into which the crucible containing the sample can be freely lowered or pulled up by means of a A.C. synchronous motor (1 rpm) and shaft arrangement. A type S thermocouple is placed on the top of the charge material to monitor the temperature change during the solidification process. The inner susceptor tube is surrounded by a set of two outer alumina tubes for radiation shielding, and supported by an alumina tube which has the same inside diameter. Between the graphite susceptor and the supporting alumina tube a ceramic baffle is used to ensure the maximum thermal gradient in the furnace. The alumina tubes rest on a flat water-cooled copper chill, with a provision at the center to effect the quenching process.

The sample was heated by means of an induction coil, which surrounds the outer quartz tube. The induction coil is a water-cooled copper coil, connected to a 5 kW, 450 kHz power supply. The top of the susceptor tube marks the beginning of the ‘hot zone’, which extends to about 140 mm. The temperature gradient, which is a very important parameter in the solidification process, was measured using a type S thermocouple. Several runs were performed to measure the temperature gradient, the measured temperature profile of the hot-zone of one typical run was presented in Figure 4-4. The average temperature gradient at the
The entire chamber was maintained at a high vacuum of about $6.67 \times 10^{-3}$ Pa ($5.0 \times 10^{-5}$ torr) using a diffusion pump and a mechanical pump. This vacuum was found to be very effective in producing samples with a very clean exterior, i.e., without any scale formation or contamination on the surface.

The crucible was lowered into the susceptor tube to the required depth (at which the temperature is well above the liquidus temperature of the alloy) by mechanically moving the shaft. Then, the chamber was evacuated using the mechanical pump and then switching on to the diffusion pump once the pressure reaches below 26.7 Pa (200 micron column of Hg read from the vacuum gauge). When chamber pressure reaches about $1.33 \times 10^{-2}$ Pa ($10^{-4}$ torr), the power is switched on. After setting the desired power level of 3.5 kW, the sample is held for half an hour under a maximum temperature of about 1773 K (1500 °C) (by this time the sample is completely liquid) and the motor is switched on. The distance moved by the sample inside the hot zone is read by converting the number of turns the shaft makes, as read by the mechanical counter, into the corresponding linear distance.

For a complete directional solidification process, after the sample has completely exited the hot zone, the power is turned off and the sample is allowed to cool (the only heat
The final directionally solidified (DS) samples were metallographically checked, and most of the samples were found to be solidified as single crystals probably because of the small diameter (about 5.0 mm); thus can be used as single crystal seeds. Pictures of these single crystal seeds (macro-etched as well as unetched) were shown in Figure 4-5.

4.5 The Ceramic Mould of SX Casting

Several SX casting trials were tried at the beginning by using the conventional investment casting shells made in Elmec, an aero-engine component repairing company in North Vancouver. Pig-tail crystal selectors attached to the ceramic shell were also tried. The investment shell should be thick to give enough strength in temperatures as high as 1773K (1500°C). In practice, due to the nature of the dipping process it was very difficult to make an investment shell with uniform outside diameters, the shell was usually found with one end approximately 1.2 times larger than another end. Because of the limited inside diameter of the graphite susceptor of the UBC Bridgman furnace, no shell could be made to suit properly the present experiments. Trials with pig-tail crystal selector were also not successful when a large enough cavity was needed. Details of the conventional investment casting trials were described elsewhere [103].

Fused alumina tubes with 25.4mm diameter were then used as ceramic crucibles (moulds) to cast the SX ingots. A ceramic plug with a Φ5.0mm hole and 75° adapter was cast at the bottom of the tubes by using a plastic pattern as shown in Figure 4-1, the material used
was the precision castable alumina ceramic RTC - 60 made by Cotronics Corporation. The crucible was dried in air for 12 hours and then in an oven at 473K (200°C) for 2 hours after casting, it was then cured in a furnace at 1223K (950°C) for two hours before use.

The SX seed was put inside the hole of the ceramic plug with its top 2 to 4 mm out of the small hole. The charge materials were placed on top of the seed inside the crucible. Due to the thermal characteristics of the UBC Bridgman furnace, stainless steel spacers had to be put between the bottom of the seed and the cooling plate of the Bridgman furnace, to make sure that the bulk charge material as well as the top of the SX seed be melted in the hot zone while the bottom of the seed is still in solid state.

The inside surfaces of the ceramic plug were observed by SEM after casting. A section of the ceramic plug was cut from the mould and sputtered with a thin gold powder in a vacuum chamber under 30 micron pressure. The roughness of the inside surface of a ceramic plug after casting was measured by using a Taylor-Hobson Stylus profilometer and a WYKO NT-2000 3D surface profiler in the Innovation Centre of National Research Council Canada, with the help of Dr. Y. Xie. Both machines gave an average roughness $Ra$ as calculated over the entire measured array, which is a straight line along the inside surface in the present case. $Ra$ is calculated per the ANSI B46.1 standard.

$$Ra = \frac{1}{n} \sum_{i=1}^{n} |Z_i - \bar{Z}|\quad (eq. \ 4-1)$$

where $n$ is the total number of points measured; $Z_i$ is the height measured at a specific point $i$; $\bar{Z}$ is the mean height.
The composition of the castable ceramic after casting was analyzed in a Rigaku diffractometer using Cu Kα radiation (λ = 1.54178 Å) in UBC. The ASTM Powder Diffraction Data File was used to distinguish the compounds contained in the castable ceramic.

4.6 The Vacuum Induction Bridgman Furnace

All the single crystal samples were directionally solidified in a vacuum induction furnace. The basic design of this furnace is similar to that of the classical Bridgman furnace used in the industry, and a schematic diagram is presented in Figure 4-6. The induction coil is connected to a 50 kW (adjustable)/4.5kHz power supply. The top lid and walls of the graphite susceptor are 30 mm thick in order to absorb over 99% of the magnetic field and prevent any electro-magnetic stirring of the melt [104]. The chamber is evacuated by a mechanical pump and a diffusion pump, and the vacuum level is consistent at 1.87 Pa (14 micron column of Hg read from the vacuum gauge). The vacuum is considered sufficiently good when cast samples would come out of the furnace without any scale or oxide “skin”.

The thermal gradient at the growth front (GL) can be adjusted from $5.0 \times 10^2$ to $8.0 \times 10^3$ K/m (5 to 80 °C /cm). It depends essentially on the withdrawal speed and on the difference between the temperature of the susceptor (the “control temperature”) and the liquidus temperature of the alloy. The solidification rate $V$ in steady-state operation is
determined by the withdrawal speed, which can be changed from $1.6 \times 10^{-5}$ to $3.4 \times 10^{-4}$ m/s (1 and 20 mm/min).

A typical experimental run follows the standard procedure outlined below:

1) The alumina crucible is filled with solid pieces of superalloy and raised into the top position inside the graphite susceptor;

2) The furnace chamber is closed and evacuated;

3) The graphite susceptor is heated up to the desired operating temperature (1733 or 1773 K) about one hour. The power is then reduced to the proper level to maintain this control temperature constant throughout the remainder of the experiment. This control temperature is chosen to set the solidification gradient to a desired value (either a low thermal gradient or a high thermal gradient);

4) The casting is allowed to reach its equilibrium temperature for an additional 2000s before it is withdrawn. Previous experiments with thermocouples inside the melt [104] showed that this period of 2000s is more than sufficient;

5) Withdrawal is started and is carried out at a constant speed for the entire length of the casting.

During the entire experiment, the furnace operating conditions (susceptor temperature, temperature alongside the casting, chill position, withdrawal speed and vacuum) are continuously monitored and recorded by a computer data acquisition system. The readers are referred to references [104, 105] for more details of this furnace.

4.7 The Validating Experiments of the ABAQUS Model

Due to the limited space inside the furnace, it is very difficult to insert thermocouples into the ingot to record the thermal history during solidification. Three trials were done to
calibrate a ABAQUS thermal model based on the commercial code ABAQUS at three different solidification speeds of 5.5x10^{-5} \text{ ms}^{-1} (3.3 \text{ mm/min}), 1.7x10^{-4} \text{ ms}^{-1} (10.0 \text{ mm/min})
and 2.5x10^{-4} \text{ ms}^{-1} (15.0 \text{ mm/min}) respectively. Two thermocouples were implanted into the transition section and the bulk section of the ingots through the mould wall in each of the trials. A single hole fused alumina tube with one end close was used as the sheath to protect thermocouple heads. Two-hole fused alumina tubes were used to insulate the thermocouple wires from each other. The gap between the mould wall and the alumina sheath was sealed with the same castable ceramic powders as those used for the ceramic plugs inside the mould. The 2 thermocouples were located along the centerline of the ingot. In the ingot cast at a rate of 5.5x10^{-5} \text{ ms}^{-1}, the locations of the two thermocouples were 43mm and 79 mm from the bottom of the seed respectively, as shown Figure 4-7. In the remaining 2 ingots, the locations of the two thermocouples were 60mm and 90 mm from the bottom of the seed respectively.
Table 4-1 Composition of Normal IN718 and IN718PSQ

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nominal Composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN718</td>
<td>0.46Al, 0.031C, 0.2Co, 18.12Cr, 2.96Mo, 5.27Nb, 53.46Ni, 1.0Ti, 0.08Si, 18.24Fe</td>
</tr>
<tr>
<td>IN718PSQ</td>
<td>0.56Al, 0.06C, &lt;0.05Co, 19.44Cr, 3.03Mo, 5.02Nb+Ta, 52.65Ni, 1.0Ti, &lt;0.02Si, 0.04B, 0.0012N, 0.0003O, Bal. Fe</td>
</tr>
</tbody>
</table>

* Alloys provided by: Special Metal Corp. (normal IN718); Canon Muskegon Corp. (IN718PSQ).
Figure 4-1 A cylinder casting sample and its plastic pattern.
Figure 4-2. IN718 casting samples with different adapter angles. While the sample with a 45° adapter (a) totally failed to produce single crystal due to the nucleation of stray grains at the top of the adapter, the one with 75° adapter produced single crystal cylinder with only minor stray grains obviously originating from surface defects.
Figure 4-3. Schematic of the DSQ furnace.
Figure 4-4. Temperature profile along the centerline of induction coil of the DSQ furnace with a 2.5 kW power output.
Figure 4-5. Single crystal seeds made in DSQ furnace, a) an unetched sample, b) an etched longitudinal section of the sample.
Figure 4-6. Schematic diagram of the Bridgman-type furnace used in this study. (105)
Figure 4-7 Ingot cast to validate the ABAQUS model showing the locations of thermocouples.
Chapter 5 Process Modeling

In order to estimate the actual solidification conditions \( (G, V \) and the liquidus isothermal curve) at various locations inside the sample, a two-dimensional numerical model of the experimental furnace was developed using the commercial finite element code ABAQUS. The goal of this model was to enable, after proper calibration, the desired translation from furnace operation parameters to actual solidification conditions in the casting, for each experiment.

ABAQUS is a product developed by Hibbitt, Karlsson & Sorensen, Inc. (HKS) for stress, heat transfer, and other types of analysis in mechanical, structural, civil, biomedical, and related engineering applications. The ABAQUS model applied to the present project is a pure uncoupled heat transfer problem. In the early stage of the present project, the ABAQUS code was run at a Silicon Graphics, Inc.'s (SGI) UNIX workstation in the Department of Metals and Materials Engineering of UBC. It was later run on a HP machine in a UNIX system of ALSTOM (Switzerland) Ltd.

Before using ABAQUS for the FE analysis, a geometry model of the furnace was created by using the commercial code PATRAN. The geometry used in the model corresponds accurately to the geometry and dimensions of the furnace, as it has been presented in Figure 5-1. The axisymmetric mesh of the whole furnace and an enlargement of the hot zone can be seen in Figure 5-1(a) and (b) respectively. Because most of the top part of the chamber is masked off by the baffle and assembly and will therefore play only a minimal role
in the view factor calculation, it has not been included in the meshing of the radiation enclosure.

The susceptor, baffle and furnace walls were considered to form a "radiation enclosure". Each of these elements was assigned a given emissivity and temperature. The copper chill, copper water-cooling pipes, steel spacer, alumina crucible and superalloy casting were modeled as independent bulk materials. All elements were meshed with 4-node linear two-dimensional solid elements DCAX4. There were 919 nodes and 658 elements in total created. Six interfaces have been defined: copper chill/water pipes, copper chill/steel spacer, copper chill/alumina crucible, steel spacer/alumina crucible, steel spacer/superalloy casting, and superalloy casting/alumina Crucible. (Figure 5-2). The relevant material property data, and the relevant boundary and initial conditions were input in PATRAN as well.

The PATRAN geometry file was then exported as an ABAQUS version 6.2 input file. The data adopted for the various interfacial heat transfer coefficients, material emissivities and temperature constraints were entered directly into the ABAQUS input file. Table 5-1 and Table 5-2 summarize all the material property, boundary and initial conditions for the various materials. The latent heat of IN718 was taken from a NPL database.

The directional solidification process was simulated in ABAQUS Standard as a cavity radiation problem, in which view factors were automatically updated by the model in order to accurately compute the radiation heat transfer, which is dependent on the relative positions of the various furnace parts. Two ABAQUS "load steps" were used in the simulation. The heating up of the ceramic crucible and superalloy casting were simulated in the first step until
a steady state is achieved, the withdrawal and hence directional solidification of the ingot was simulated in a second step. As an example, the input file for casting with a withdrawal speed of $5.4 \times 10^{-5} \text{ ms}^{-1}$ (3.3 mm/min) together with its input data files were given in Appendix A. The liquid temperature gradient at the liquid/solid interface and the velocity of the isothermal line of liquidus were calculated along the centre line of the casting ingot. A user defined subroutine was used for this calculation, in which the global heat flux was divided by the thermal conductivity. The temperature gradient calculated is therefore the global gradient. The vertical coordinate of integration node along the ingot centre line was recorded when its temperature reached the liquidus temperature (ie. $1336^\circ \text{C} \leq \text{Temp} \leq 1336.2^\circ \text{C}$). The subroutine is given in Appendix B. For detailed FE calculation techniques, the readers are referred to ABAQUS manuals [106].

The post-analysis was executed in ABAQUS/Viewer, which is the interactive postprocessor for ABAQUS. ABAQUS/Viewer provides deformed configuration, contour, vector, and X-Y plots, as well as animation of results.

The model parameters have been calibrated with thermocouple measurements in the experimental furnace. The $G$ and $V$ values calculated from the simulation showed little sensitivity to most of the parameters in the model which had to be estimated (emissivities, surface temperatures, heat transfer coefficients).
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Location</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat</td>
<td>Chill / Pipes</td>
<td>4500</td>
</tr>
<tr>
<td></td>
<td>Chill / Spacer</td>
<td>400</td>
</tr>
<tr>
<td>Transfer</td>
<td>Chill / Alumina tube</td>
<td>200</td>
</tr>
<tr>
<td>Coefficient</td>
<td>Spacer / Alumina tube</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>Spacer / Casting</td>
<td>300</td>
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<tr>
<td>(Wm$^{-2}$K$^{-1}$)</td>
<td>Casting / Crucible (at solidus)</td>
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<tr>
<td></td>
<td></td>
<td>100, 600°C</td>
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<td></td>
<td></td>
<td>180, 800°C</td>
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<tr>
<td></td>
<td></td>
<td>200, 924°C</td>
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<tr>
<td></td>
<td></td>
<td>700, 1260°C</td>
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<td></td>
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<td>1000, 1336°C</td>
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<tr>
<td></td>
<td></td>
<td>8480, 2000°C</td>
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<tr>
<td>Emissivities (-)</td>
<td>Copper (baffle, chill)</td>
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<td></td>
<td>Chamber walls</td>
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<td>Alumina tube</td>
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<td></td>
<td>Superalloy casting (liquid)</td>
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<tr>
<td></td>
<td>Graphite</td>
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<tr>
<td>Temperature (K)</td>
<td>Baffle top</td>
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<tr>
<td>Assigned to Enclosure</td>
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<td>Water pipes</td>
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<tr>
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<td>Superalloy casting</td>
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<tr>
<td>Initial Temperature (K)</td>
<td>Alumina tube</td>
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</tr>
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<td></td>
<td>Steel spacer</td>
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<tr>
<td></td>
<td>Water cooled copper chill</td>
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<tr>
<td>Properties</td>
<td>Ni-based superalloy (casting)</td>
<td>Fused Alumina (crucible)</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
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<td>3970</td>
</tr>
<tr>
<td></td>
<td>7800</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7400</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7300 [105]</td>
<td></td>
</tr>
<tr>
<td>Specific Heat (kJ/kg.K)</td>
<td>21°C 0.43</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>538°C 0.56</td>
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<tr>
<td></td>
<td>871°C 0.65</td>
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</tr>
<tr>
<td></td>
<td>1600°C (0.84) [105]</td>
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</tr>
<tr>
<td>Conductivity (W/m.K)</td>
<td>21°C 11.40</td>
<td>200°C 22.0</td>
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<tr>
<td></td>
<td>1260°C 25.00</td>
<td>400°C 13.0</td>
</tr>
<tr>
<td></td>
<td>1336°C 26.00</td>
<td>600°C 9.3</td>
</tr>
<tr>
<td></td>
<td>1400°C 40.00</td>
<td>800°C 7.3</td>
</tr>
<tr>
<td></td>
<td>1450°C 180.00</td>
<td>1000°C 6.2</td>
</tr>
<tr>
<td></td>
<td>1600°C 200.00</td>
<td>1600°C (3.0)[105]</td>
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<tr>
<td>Latent Heat (kJ/kg)</td>
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<td>N/A</td>
</tr>
<tr>
<td>Emmissivity (-)</td>
<td>0.9</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Figure 5-1 Axisymmetric mesh geometry used in ABAQUS to model the furnace.
Figure 5-2. Schematic heat flow diagram in the ABAQUS model of the experimental furnace.
Chapter 6 Experiment and Thermal Model Results

6.1 Nitrogen Content of the Alloys

The analyzed oxygen and nitrogen content were given in Table 6-1. It can be seen that the analyzed [N] content of IN718PSQ agrees very well with the nominal composition given in Table 4-1, the analyzed [N] content of normal IN718 is among the usual industry range for IN718 alloys. Because the raw materials of IN718PSQ and normal IN718 were cast as supplied, the [N] level of IN718PSQ and normal IN718 used in the present research are considered as the analyzed level given in Table 6-1, which are <10 ppm and ~47 ppm respectively. The high [N] content of IN718N were obtained by adding chromium nitrides, so five of the seven IN718N samples were analyzed. It was found that the addition of chromium nitride particles successfully increased the [N] level of alloys to a much higher level than the equilibrium solubility of [N] in IN718 at the liquidus (eg. 39 ppm). The [N] content of the other three samples SX101 and EX101 was taken as the average, i.e. 86 ppm.

6.2 Oxygen Content of the Alloys

The [O] content of all the alloys were controlled to a very low level by using low oxygen content raw materials in order to eliminate the effects of oxide inclusions such as Al₂O₃, MgO etc. in the liquid. However the analyzed [O] content of all the three alloys was higher than the nominal content of raw materials, for example, as high as 27 PPM [O] content was analyzed for alloy IN718PSQ with a nominal [O] content of 3 PPM. The error was due to
the contamination during cutting of the analysis samples by using the SiC wheel blade. The samples were cooled by the coolant during cutting, however experience tells that the cooling is usually not efficient, consequently an oxygen level of about 25 PPM could be easily introduced by the oxidation in the high temperature caused by friction during cutting. Therefore the actual [O] content was believed to be much lower than the analysis results.

6.3 Crystallographic Orientation of the SX Seeds

The primary dendrites of most seeds were not parallel to their vertical axis. A typical condition was clearly shown in Figure 4-5 b); this direction deviation can also be clearly observed in seeds after casting as shown in Figure 6-3, Figure 6-20 and Figure 6-22. The direction of primary dendrites of the SX seeds was found to be 20-40 degrees from the vertical axis. Observations of the deviation of the primary dendrite direction from the vertical axis (crystal growth direction) in the bulk section of the castings are given later in this chapter.

6.4 Mould Surface and Composition

Roughness of the post-casting inside surface of the alumina cement insert was measured and the results are shown in Table 6-2, it can be seen in Figure 6-1 that pores and cracks appeared on the inside surface of ceramic plugs. The pores and cracks caused a very rough surface in the tapered section. It is possible that the nucleation of new grains often found in this area was caused by these surface defects, see for example in Figure 4-2b). Figure 6-2 gives the X-ray diffraction analysis results. The castable ceramic cement after use, was
found to be a mixture of compounds $\text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$.

6.5 Crystal Structure of the Castings

Samples of IN718 alloys with low, normal and high nitrogen content were cast at control temperatures of 1773K (1500°C) or 1733K (1460°C) with withdrawal speeds ranging from $1.7 \times 10^{-5}$ to $3.4 \times 10^{-4}$ ms$^{-1}$ (1 to 20.1mm/min). The casting parameters, as well as the crystal structure observed from the macro-etched surface and longitudinal section, are given in Table 6-3, Table 6-4 and Table 6-5 for samples of IN718PSQ, normal IN718 and IN718N respectively. The detailed description was given as below.

6.5.1 Low [N] IN718

Figure 6-3 and Figure 6-4 show the bi-crystal structure of two samples with low nitrogen content (IN718PSQ) PSQ003 and PSQ006, both of which were cast under low solidification velocities ($\leq 4.7 \times 10^{-5}$ ms$^{-1}$ (2.8mm/min)). The secondary grain originated from the transition part of the casting and grew together with the primary grain. It can be seen from Figure 6-3a) that the primary grain of the casting has a crystallographic orientation very similar to that of the SX seed, therefore the bi-crystals were considered as SX structure as is often the case in the SX turbine blade industry. A similar bi-crystal structure was observed in the IN718N sample SX101, which was cast at a low withdrawal speed ($1.8 \times 10^{-5}$ ms$^{-1}$).

IN718PSQ samples cast under mid-range velocities (from $1.1 \times 10^{-4}$ ms$^{-1}$ to $1.7 \times 10^{-4}$ ms$^{-1}$ (6.4 to 10 mm/min)) show the SX crystal structure at the bottom and multi-crystal
columnar structure at the top of the casting. More than one columnar grain were found in addition to the large primary columnar grains that developed from the SX seed. Most of the small grains were found at the side instead of center of the casting, as shown in Figure 6-5 and Figure 6-6. The structure of these samples was labeled as SX to CX (single crystal to columnar) structure in Table 6-3 and Figure 6-7.

The IN718PSQ sample cast under the highest solidification velocity (3.4 x 10^{-4} \text{ ms}^{-1} (20.5 \text{ mm/min})) showed a bi-crystal structure as shown in Figure 6-8. Figure 6-8c shows an enlarged picture of the SX seed, it can be seen that, not like IN718PSQ samples cast at lower speed (PSQ003 and PSQ006), the second crystal of PSQ002 originated from the top part of the seed instead of the adapter section of the casting. The orientations of the primary dendrites of these two grains are quite different as shown in Figure 6-8d, therefore this bi-crystal is considered as a multi columnar crystal structure.

The change of crystal structure of IN718PSQ samples was plotted along with the solidification velocity and nitrogen content in Figure 6-7, in which the nitrogen content of sample PSQ003 and PSQ005 were taken from analysis results given in Table 6-1. Since the raw material used was from the same ingot of IN718PSQ sent by the sponsors, an average value (10 PPM) of the analysis results was used as the nitrogen content of other IN718PSQ samples in Figure 6-7. It can be seen from Figure 6-7 that the crystal structure of castings changed with the increasing solidification velocity. Samples cast at low solidification velocities have a SX or bi-crystal structure, whereas samples cast at higher solidification velocity transition from SX structure to a multi-crystal columnar structure (labeled as SX to
CX in Table 6-3). No EQ grains were found in all the IN718PSQ samples.

6.5.2 Normal IN718

Figure 6-9 to Figure 6-19 show the grain structure of typical samples of normal IN718. There were more samples of normal IN718 cast at low solidification velocity ($\leq 4.7 \times 10^{-5}$ ms$^{-1}$ (2.8mm/min)) than the other two alloys IN718PSQ and IN718N. They were cast at a control temperature of 1733K (1460°C) that is different with the 1773K (1500°C) control temperature of all other samples (see Table 6-3). This is because normal IN718 was the first alloy tested in order to find the correct casting procedure for SX samples in the UBC Bridgman furnace.

It was found in the first round of the casting trial, the crystal structure of castings was affected by factors other than the alloy composition and the melting and casting parameters. As mentioned previously in section 6.5.1 above, spurious grains could be found nucleated on the rough mould surface. Multi columnar crystal structures were also found originating from the top part of SX seeds in samples SX007 and SX009, as clearly shown in Figure 6-12 and Figure 6-14 respectively.

However, all other normal IN718 samples cast at low solidification velocity were found with a mixed structure of a large primary crystal grown from the SX seed and some small columnar crystals that have diameters less than 5 mm and lengths much less than the whole length of the casting. The crystal structure of sample SX003, SX004, SX005 and SX008 were shown in Figure 6-9, Figure 6-10, Figure 6-11 and Figure 6-13 respectively. All of the small columnar crystals observed in the samples originated at the tapered section of the
samples. Figure 6-10b shows that the small crystals appeared at the side but not the center of the casting sample.

Normal IN718 samples SX202, SX201, SX203 and EX011 were cast at higher solidification velocities ($\geq 1.1 \times 10^{-4}$ ms$^{-1}$ (6.4 mm/min)), their crystal structures were shown in Figure 6-15, Figure 6-16, Figure 6-17 and Figure 6-18 respectively. A structure transition from SX to CX was observed in all these samples. The multi-crystal columnar structure, which originated at the tapered section of the samples, were usually much larger than those in the samples cast at low velocities and grew through the whole length of the casting. They appeared at the side but not the center of the samples, like those found in the low solidification speed samples.

Sample EX001 was cast without SX seed at the bottom at the speed of $3.4 \times 10^{-4}$ ms$^{-1}$ (20.5 mm/min). As shown in Figure 6-19, a multi-crystal columnar structure was found throughout the whole sample, including the small extension at the bottom of the sample, which was usually the location of SX seeds in other samples. No equiaxed grains was found in either the side or the center of the sample.

As for IN718PSQ samples, the change of crystal structure of normal IN718 samples was plotted along the solidification velocity and nitrogen content in Figure 6-7. The nitrogen content of sample SX004 and EX011 was taken from analysis results given in Table 6-1. Since the raw material of all IN718 samples was from the same ingot of IN718, like those of alloy IN718PSQ samples, an average value (47PPM) of the analysis results was considered as the nitrogen content of the other normal IN718 samples. It can be seen from Figure 6-7 that
the crystal structure of castings changed with the increasing solidification velocity. Samples cast at low solidification velocities have a SX or bi-crystal structure, whereas samples cast at higher solidification velocity have a transition from SX structure to multi columnar crystal structure (labeled as SX to CX in Table 6-3, Table 6-4, Table 6-5 and Figure 6-7). Sample EX001 was not included in Figure 6-7, because it was not cast with a SX seed and therefore had different crystal growth conditions from the others. No EQ grains were found in all the IN718 samples.

6.5.3 High \([N]\) Content IN718

Figure 6-20 to Figure 6-26 show the grain structure of the cast samples with high nitrogen content (IN718N). Like the samples of IN718PSQ and normal IN718, samples of IN718N cast at low solidification velocity ($\leq 4.7 \times 10^{-5} \text{ms}^{-1}$ (2.8mm/min)) showed structures of SX/bi-crystal or a mix of one or two columnar grains (~2mm in diameter and <4mm in height) with a large crystal grown from the SX seed. Figure 6-20 shows the SX/bi-crystal structure of SX101. The secondary grain originated from the transition part of the casting and grew competitively with the primary grain. It is difficult to distinguish the two crystals from the longitudinal section of the sample in Figure 6-20a, because the difference in the orientations of the primary dendrites of the two crystals are very small; however a sub-grain-boundary was clearly observed in the cross section in Figure 6-20 b. It can also been seen that the primary dendrite orientation of the crystal (usually the $<001>$ direction for Ni base superalloys) deviated from the vertical axis of casting (z axis) by an angle of about 40°, which agrees very well with the orientation of the primary dendrite of the SX seed.
Two small columnar grains were found on the side of sample MX301 originating in the transition section of the sample. However the main body of the casting is a single crystal grown from the SX seed. As shown in Figure 6-21, the primary crystal has the same dendrite orientation as the top section of the SX seed.

IN718N sample (MX201) cast at a mid-range velocity (1.1 x 10^{-4} \text{ ms}^{-1} (6.4 \text{ mm/min})) formed a similar crystal structure as samples of the other two alloys IN718PSQ and normal IN718 cast in the same velocity range. Large columnar crystals originated within the tapered section of the sample which grew together with the primary crystal (formed from the SX seed) through the whole length of the casting. These columnar crystals were also found on the side of the sample only (Figure 6-22). However, at least one equiaxed crystal was found at the center of the sample as shown in Figure 6-22b.

Sample MX101 was cast at a slightly higher solidification velocity (1.7 x 10^{-4} \text{ ms}^{-1} (10.0 \text{ mm/min})) and formed columnar crystals on the side of the sample. However these side columnar crystals were short and did not grow through the whole length of the casting. Furthermore, a continuing cluster of EQ grains was found along the center-line of the sample as shown in Figure 6-23b.

The crystal structure of IN718N samples cast at the higher solidification velocities (from 2.1 x 10^{-4} \text{ ms}^{-1} to 3.4 x 10^{-4} \text{ ms}^{-1} (12.5 to 20.5 \text{ mm/min})) changed drastically. Initially, SX/bi-crystal structure was developed from the SX seed, then the SX/bi-crystal growth was totally converted into an EQ structure at the middle of the tapered section of the castings. The
equiaxed grains have a diameter about 0.5 cm. The average grain size and the grain size
distribution of the EQ grains varied with solidification velocity. Sample MX501 was cast at a
slightly lower solidification velocity. It can be found from Figure 6-24 that the size of EQ
gains along the casting center-line of MX501 is quite uniform and is smaller than the size of
those side grains. The size of EQ grains in MX401 and EX101 became quite uniform as
shown in Figure 6-25 and Figure 6-26. However the average EQ grain size of MX401, which
was cast at solidification velocity of $2.6 \times 10^{-4}$ ms$^{-1}$ (15.5 mm/min), is slightly larger than that
of EX101, which was cast at the highest velocity of $3.4 \times 10^{-4}$ ms$^{-1}$ (20.5 mm/min). It is note
worthy that a SX structure was developed from the SX seed in both MX501 and EX101,
however a bi-crystal instead of SX structure was developed at the same location in MX401.
As can be clearly seen from Figure 6-25b, the bi-crystal originated inside the SX seed, thus
was not considered to be a consequence of the solidification variables. Therefore this bi-
crystal was labeled as SX in Figure 6-7, although it was distinguished as bi-crystal in Table
6-5.

As for IN718PSQ and normal IN718 samples, the change of crystal structure of
IN718N samples was plotted along the solidification velocity and nitrogen content of samples
in Figure 6-7. The nitrogen content of sample MX101, MX201, MX301, MX401 and MX501
were taken from analysis results given in Table 6-1. Because the raw materials of all IN718N
samples were taken from the same ingot, and chromium nitride powders were added to the
sample with the same nitrides/bulk ratio, the average nitrogen content (86 PPM) of the
analyzed 5 samples was used as the nitrogen content of samples SX101, SX102 and EX101 in
Figure 6-7. It can be seen from Figure 6-7 that the crystal structure of castings changed with
the increasing solidification velocity. Samples cast at low solidification velocities (SX101, SX102 and MX301) have a SX/bi-crystal structure. Samples cast at mid-range solidification velocities (MX201 and MX101) have a transition from SX structure to multi columnar crystal structure (labeled as SX to CX in Table 6-3, Table 6-4, Table 6-5 and Figure 6-7), isolated EQ grains (MX201) or a continuing EQ grain cluster was found at the center-line of these samples. A breakdown of the SX/bi-crystal by EQ grain structure occurred in IN718N samples cast at higher solidification velocities.

6.5.4 Validation Trials of the ABAQUS Model

Two thermocouples were used to record the cooling profile of two points along the centerline of the ingots. Three such trials have been done and the results were shown in Figure 6-27, Figure 6-28 and Figure 6-29 for ingot cast at solidification speeds of 5.5x10^{-5} \text{ ms}^{-1} (3.3 \text{ mm/min}), 1.7x10^{-4} \text{ ms}^{-1} (10.0 \text{ mm/min}) and 2.5x10^{-4} \text{ ms}^{-1} (15.0 \text{ mm/min}) respectively. In the ingot cast at a rate of 5.5x10^{-5} \text{ ms}^{-1}, the locations of the two thermocouples were 43mm and 79 mm from the bottom of the seed respectively. In the remaining 2 ingots, the locations of the two thermocouples were 60mm and 90 mm from the bottom of the seed respectively. Results shown in Figure 6-28 and Figure 6-29 were considered unsuccessful, because in both cases thermocouples at higher locations (90mm) gave lower temperature readings than those at lower locations (60mm) in the middle of the solidification, which is obviously inconsistent with the fact the ingots were cooled directionally from the bottom to the top. Therefore only the results obtained in the ingot cast at solidification speed of 5.5x10^{-5} \text{ ms}^{-1} (3.3 \text{ mm/min}) was considered usable.
6.5.5 Summary of Experimental Results

1. When cast at low solidification velocity \((\leq 4.7 \times 10^5 \text{ms}^{-1}) (2.8 \text{mm/min})\), samples of IN718 with all three nitrogen contents (<10, ~47 and ~86 PPM) developed a SX/bi-crystal structure from the SX seed, except for sample SX005, SX007 and SX009 of normal IN718;

2. When cast at higher solidification velocities \((\geq 1.1 \times 10^4 \text{ms}^{-1}) (6.4 \text{mm/min})\), samples (IN718PSQ and normal IN718) with low nitrogen content \((\leq 47\text{PPM})\) showed similar crystal structure transition from SX/bi-crystal to multi columnar crystal. No EQ grains could be found in these samples;

3. In samples (IN718N) with nitrogen content much higher than the nitrogen equilibrium solubility \((\text{e.g. } 86\text{PPM})\) cast at the same solidification velocity range mentioned above \((\geq 1.1 \times 10^4 \text{ms}^{-1}) (6.4 \text{mm/min})\), EQ grains were found and their number increased gradually with the solidification velocity;

4. When cast at the lower end of the aforementioned solidification range, i.e. from 1.1 x \(10^4 \text{ ms}^{-1}\) (6.4 mm/min) to 1.7 x \(10^4 \text{ ms}^{-1}\) (10.0 mm/min), samples (IN718N) with nitrogen content much higher than the nitrogen equilibrium solubility \((\text{e.g. } 86\text{PPM})\) showed mainly a transition from SX/bi-crystal to multi columnar crystal structure, EQ grains occurred in the center line of castings;

5. When cast at the higher end of the aforementioned solidification range, i.e. above 1.7
x $10^{-4}$ ms$^{-1}$ (10.0 mm/min), samples (IN718N) with nitrogen content much higher than the nitrogen equilibrium solubility (e.g. 86PPM) showed a structure breakdown of SX/bi-crystal by EQ grains. With the increase of solidification velocity, the EQ grains size became more uniform and the average grain size decreased.

6. In ingots with a CX structure, the CX grains along the center line usually have the same orientation as the SX seed, while CX grains in both sides of the longitudinal section of a casting ingot grow towards the center.

6.6 **ABAQUS Model Results**

The ABAQUS model was carefully calibrated with experimental data measured in the validation trial with a solidification speed of $5.5 \times 10^{-5}$ ms$^{-1}$ (3.3 mm/min), as indicated previously. The main thermal parameters like the heat transfer coefficients in the interfaces between different materials were finely tuned to give the best fit between calculated and measured cooling profiles. The results were shown in Figure 6-30. A reasonable match can be found between the calculated and measured data to within approximately ±20%, which serves as an estimate of the error in the calculation. The ABAQUS model was then considered valid to simulate the solidification process of the present project.

Once validated, the model was used to estimate liquid temperature gradients at solid/liquid interface (at the liquidus temperature of IN718, 1609K) under various solidification conditions in the middle of the transition section of the ingot (vertical coordinate $Y = 74.6$ mm), where the grain structure transition was typically observed to occur, as described previously. The calculation results were given in Table 6-3, Table 6-4 and Table 86.
6-5 for IN718PSQ, normal IN718 and IN718N samples, respectively. The range of the interface temperature gradient was found to be $3.1 \times 10^3$ K/m to $7.5 \times 10^3$ K/m. The vertical coordinate ($Y$) of the liquidus isotherm along the center-line was extracted from ABAQUS model and plotted against time for each withdrawal rate. In all of the cases, it was found, the $Y$ vs. time plot forms a straight line when $Y$ goes above 70 mm, as shown in Figure 6-31 as an example. In other words, the solidification velocity becomes stable and consistent after the S/L isotherm reaches a certain height (in this case 70 mm), which was a phonon that has been observed before [31, 104].

The moving velocity of liquidus isotherm was then calculated from the slope of the plot of $Y$ vs. time line. The results for solidification velocity, or the velocity of liquidus isotherm, were also given in Table 6-3, Table 6-4 and Table 6-5. The interface temperature gradient decreased with increasing of withdrawal rate. Two control temperatures (hot-zone temperatures) were used in the experiments, and it is worth noting that the lower control temperature (1733K) produced a significantly lower interface temperature gradient in samples cast at the same withdrawal rate. For example, for a withdrawal rate $1.8 \times 10^{-5}$ m/s, sample SX101, cast at control temperature 1773K, had an interface temperature gradient of 7890.5K/m, while sample SX009, cast at control temperature 40K lower, had an interface temperature gradient of 6625.4K/m only.

The liquid/solid interface curve was also calculated for every sample using ABAQUS. The interface curve for samples cast at rate $1.8 \times 10^{-5}$, $16.2 \times 10^{-5}$ and $34.2 \times 10^{-5}$ m/s are shown in Figure 6-32, Figure 6-33 and Figure 6-34, respectively. It can be seen that the liquid/solid
interface is almost flat at low solidification rate, however the curvature increases gradually with solidification rate and becomes very obvious at velocities above $16.2 \times 10^{-5} \text{m/s}$, even in ingots with a diameter of only 0.0254m as in the present case. In addition, the height of mushy zone is found to increase with the solidification rate, consistent with the decrease in thermal gradient that observed with increasing withdrawal rate.
Table 6-1 Oxygen and Nitrogen Content of Samples Analyzed in Allvac.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sample No.</th>
<th>[O] (PPM)</th>
<th>[N] (PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN718N</td>
<td>MX101</td>
<td>27</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>MX201</td>
<td>13</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>MX301</td>
<td>21</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>MX401</td>
<td>38</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>MX501</td>
<td>34</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>SX004</td>
<td>19</td>
<td>44</td>
</tr>
<tr>
<td>Normal IN718</td>
<td>SX011</td>
<td>15</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>PSQ003</td>
<td>27</td>
<td>9</td>
</tr>
<tr>
<td>IN718PSQ</td>
<td>PSQ005</td>
<td>22</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 6-2 Roughness of the Post-casting Inside Surface of Ceramic Plugs Measured by Two Machines

<table>
<thead>
<tr>
<th></th>
<th>Stylus Profilometer</th>
<th>3D surface profiler</th>
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<tr>
<td></td>
<td>2.68 μm</td>
<td>2.23 μm</td>
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### Table 6-3 Casting Parameters and Crystal Structure of IN718PSQ Samples.

<table>
<thead>
<tr>
<th>Vac. (μ)</th>
<th>T_Ctrl (K)</th>
<th>Withdrawal Rate (10^{-5} m/s)</th>
<th>Solidification Velocity (10^{-5} m/s)</th>
<th>Sample No.</th>
<th>Microstructure</th>
<th>Transition Location</th>
<th>Temp. Grad. (K/m) (±20%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>1773</td>
<td>3.0</td>
<td>3.9</td>
<td>PSQ003</td>
<td>SX</td>
<td>-</td>
<td>7515.1</td>
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<tr>
<td></td>
<td></td>
<td>4.7</td>
<td>5.9</td>
<td>PSQ006</td>
<td>SX</td>
<td>-</td>
<td>7069.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.7</td>
<td>12.5</td>
<td>PSQ005</td>
<td>SX to CX plus small spurious columnar grains</td>
<td>Middle of the tapered section</td>
<td>5690.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.7</td>
<td>19.5</td>
<td>PSQ004</td>
<td></td>
<td>Lower part of the tapered section</td>
<td>4705.2</td>
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<tr>
<td></td>
<td></td>
<td>34.2</td>
<td>42.0</td>
<td>PSQ002</td>
<td>CX</td>
<td>-</td>
<td>3062.8</td>
</tr>
</tbody>
</table>

### Table 6-4 Casting Parameters and Crystal Structure of Normal IN718 Samples.

<table>
<thead>
<tr>
<th>Vac. (μ)</th>
<th>T_Ctrl (K)</th>
<th>Withdrawal Rate (x10^{-5} m/s)</th>
<th>Solidification Velocity (10^{-5} m/s)</th>
<th>Sample No.</th>
<th>Microstructure</th>
<th>Transition location</th>
<th>Temp. Grad. (K/m) (±20%)</th>
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</thead>
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<tr>
<td>14</td>
<td>1733</td>
<td>4.2</td>
<td>5.4</td>
<td>SX001</td>
<td>SX or bi-crystal with small spurious columnar grains</td>
<td>-</td>
<td>6142.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.2</td>
<td>5.4</td>
<td>SX002</td>
<td>SX or bi-crystal with small spurious columnar grains</td>
<td>-</td>
<td>6142.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>3.3</td>
<td>SX003</td>
<td>SX or bi-crystal with small spurious columnar grains</td>
<td>-</td>
<td>6487.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>3.3</td>
<td>SX004</td>
<td>SX or bi-crystal with small spurious columnar grains</td>
<td>-</td>
<td>6487.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>3.3</td>
<td>SX005</td>
<td>SX or bi-crystal with small spurious columnar grains</td>
<td>-</td>
<td>6487.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>2.0</td>
<td>SX008</td>
<td>SX or bi-crystal with small spurious columnar grains</td>
<td>-</td>
<td>6704.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.2</td>
<td>-</td>
<td>SX007</td>
<td>CX</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.8</td>
<td>2.4</td>
<td>SX009</td>
<td>CX</td>
<td>-</td>
<td>6625.4</td>
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<tr>
<td></td>
<td>1773</td>
<td>10.8</td>
<td>12.6</td>
<td>SX0205</td>
<td>SX to CX, transition occurred</td>
<td>bottom of the adapter section</td>
<td>5664.1</td>
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<tr>
<td></td>
<td></td>
<td>16.2</td>
<td>19.0</td>
<td>SX0201</td>
<td>SX to CX, transition occurred</td>
<td>bottom of the adapter section</td>
<td>4768.8</td>
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<tr>
<td></td>
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<td>27.5</td>
<td>33.3</td>
<td>SX203</td>
<td>SX to CX, transition occurred</td>
<td>middle of the adapter section</td>
<td>3557.5</td>
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<td></td>
<td></td>
<td>34.2</td>
<td>42.0</td>
<td>EX001</td>
<td>SX to CX, transition occurred</td>
<td>middle of the adapter section</td>
<td>3062.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>34.2</td>
<td>42.0</td>
<td>EX011</td>
<td>SX to CX, transition occurred</td>
<td>middle of the adapter section</td>
<td>3062.8</td>
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</table>
Table 6-5 Casting Parameters and Crystal Structure of IN718N Samples.

<table>
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<tr>
<th>Vac. (μ)</th>
<th>T_{ctrl} (K)</th>
<th>Withdrawal Rate (x10^{-5} m/s)</th>
<th>Solidification Velocity (x10^{-5} m/s)</th>
<th>Sample No.</th>
<th>Microstructure</th>
<th>Transition location</th>
<th>Temp. Grad. (K/m) (±20%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 N₂</td>
<td>1773</td>
<td>1.8</td>
<td>2.4</td>
<td>SX101</td>
<td>SX or bi-crystal with small spurious columnar grains</td>
<td>-</td>
<td>7890.5</td>
</tr>
<tr>
<td></td>
<td>800 ~1000 N₂</td>
<td>4.7</td>
<td>5.9</td>
<td>MX301</td>
<td></td>
<td>-</td>
<td>7069.4</td>
</tr>
<tr>
<td></td>
<td>16.7</td>
<td>10.7</td>
<td>12.5</td>
<td>MX201</td>
<td>SX to CX with one or more EQ along centerline,</td>
<td>middle of the adapter section</td>
<td>5690.1</td>
</tr>
<tr>
<td></td>
<td>20.8</td>
<td>16.7</td>
<td>19.5</td>
<td>MX101</td>
<td>SX to CX with continuing EQ cluster along centerline</td>
<td>In the adapter section</td>
<td>4705.2</td>
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<td></td>
<td>25.8</td>
<td>20.8</td>
<td>24.5</td>
<td>MX501</td>
<td>Larger size EQ breakdown of SX</td>
<td>middle of the adapter section</td>
<td>4190.7</td>
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<tr>
<td></td>
<td>34.2</td>
<td>30.8</td>
<td>42.0</td>
<td>MX401</td>
<td>Small size EQ breakdown of bi-crystal</td>
<td></td>
<td>3652.0</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>EX101</td>
<td>Small size EQ breakdown of SX</td>
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<td>3062.8</td>
</tr>
</tbody>
</table>
Figure 6-1 SEM image of the rough inside surface of ceramic plugs after casting showing porosity holes on the surface.
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Chapter 7 Analysis of Experimental Results

7.1 The Nucleation of Multi Columnar Crystals

Secondary columnar crystals were found nucleated at the remelted top part of SX seeds (PSQ002, SX007, SX009, MX101 and MX401), at the tapered section of castings (PSQ006, PSQ005, PSQ004, SX003, SX004, SX005, SX008, SX202, SX201, SX203, EX011, MX301, MX201 and MX301) and in the bulk section above the transition section (PSQ004 and EX011). The mechanism of the nucleation of these columnar crystals is analyzed as below.

7.1.1 Secondary Columnar Crystals Nucleated from SX Seeds

The SX seeds used for the SX casting process usually have smaller diameters than the cavity in the ceramic mould that holds them. Furthermore they are not perfect cylinders thus there are usually small gaps between the seed and the mould wall. The molten liquid metal flowed through these SX seed/mould gaps and solidified, and new crystals could nucleate and grow from this material. The growth of these stray edge crystals competing with the seed crystal may be influenced by factors such as the alloy composition, the solid-liquid interface curvature and the crystallographic orientation and its relationship with the macroscopic heat flow axis. As pointed out by D’Souza et al. [89], the angle between the <100> direction of the grain and the local normal to the curved S/L interface, designated \( \angle_{<001>} \), can be used as the main factor controlling the competition growth between the seed crystal and the secondary
crystals. Grains with a smaller $\angle_{<001>}$ angle can overgrow grains with a larger $\angle_{<001>}$ angle. Therefore, when the difference between the $\angle_{<001>}$ angle of a seed crystal and of any secondary crystals are small, or, when the secondary crystals nucleated on the seed side have a smaller $\angle_{<001>}$ than the seed crystal's, the secondary crystals will develop. As described in Chapter 5, the primary dendrite orientation of SX seeds used in the present experiments deviated 20-40 degrees from the vertical crystal growth direction, which gave a large $\angle_{<001>}$ angle assuming there was a flat liquidus isotherm. Thus, it is not surprising that more than one grain entered the transition region.

Once a secondary crystal with a small $\angle_{<001>}$ angle had formed at the top part of the seed, it can grow over the entire length of the ingot, which is the case observed in samples PSQ002, SX007 and SX009. However, both the primary SX crystals and the secondary crystals could be blocked by EQ grains, as in the case for MX101 and MX401.

7.1.2 Mold Surface Roughness and Multi Columnar Crystals Nucleated at the Bulk Section of Castings

Most of the multi columnar crystals nucleated in the transition section of the castings occurred at the surface of the samples. The ceramic plug, made of alumina cement, is not as mechanically strong as the fused alumina crucibles and is vulnerable to extensive liquid metal erosion and thermal stress cracking at temperatures above 1500°C, thus it is not surprising to find pores and deep cracks on the plug's inside surface after casting, as shown in Figure 6-1. These surface pores and cracks could be favored nucleation sites for the multi columnar
crystals. According to the X-ray diffraction analysis results, the ceramic plug contains nothing other than alumina plus alumina silicates (Figure 6-2) which have crystal lattice parameters not favorable for the nucleation of a new crystal of superalloys based on the lattice disregistry theory. Therefore, the ceramic cement itself could be eliminated as a nucleation catalyst for the multi columnar crystals.

There were also multi columnar crystals nucleated at the bulk section above the transition section in the castings but in a fewer number of samples (in samples PSQ004 and EX011 only). The surface defects could still play a role on the nucleation in this location due to the presence of surface defects in the alumina tube.

For IN718 alloys with all three different nitrogen contents, fewer and shorter multi columnar crystals could usually be found in samples cast at lower solidification velocities than in samples cast at higher solidification velocities, which could be explained by the fact that the undercooling at the solidification front increases with the solidification velocity, as further discussed later in this chapter, and more surface defects could be activated as the undercooling becomes larger. Higher solidification velocities could introduce a higher density of active nucleation sites and hence more secondary crystals. High solidification velocities could also cause a deeper concave liquidus isotherm, which will change the $\angle_{<001>}$ angle of the crystals growing from the edge. Usually secondary crystals with primary dendrites toward the centerline will have a smaller $\angle_{<001>}$ angle than those crystals outward to the centerline, hence could grow longer before they are over grown by the primary crystal. This phenomenon was clearly observed in Figure 6-5 and Figure 6-6 for samples PSQ005 and PSQ004,
respectively. There are other factors such as alloy composition that could also influence the competitive growth of secondary crystals. However, more detailed analysis of the growth competition of columnar crystals is beyond the scope of the present research.

7.2 TiN Particles and the Nucleation of EQ Grains

EQ grains were found only in high nitrogen content samples (IN718N) cast at solidification velocities higher than 1.1x10^{-4} \text{ ms}^{-1} (6.4 \text{ mm/min}). Although some IN718N samples contained higher oxygen contents than samples of IN718PSQ and normal IN718 (see Table 6-1), the difference was not marked and would likely cause no change in the formation of oxides in the liquid. Furthermore, as mentioned previously, the oxidation could have potentially occurred during the cutting of the samples. The only difference between the IN718N samples and the samples cast at the same control temperature and withdrawal speed is thus the \([N] \) content. Therefore, it is reasonable to say that the appearance of EQ grains at the solidification conditions employed by the present study was caused by a nitrogen content much higher than the equilibrium solubility of nitrogen in the liquid metal.

A content of less than 100 PPM \([N] \) would not change the liquidus and solidus of the alloys. The Cr content introduced by the addition of chromium nitrides should also only have a negligible effect on the liquidus and solidus temperatures because the Cr content of IN718 alloy is high (18.12\%). The influence of the addition of chromium nitride particles on the diffusivity and segregation behaviour of alloy elements in the liquidus temperature should also be limited and negligible. Therefore, any solidification behaviour difference caused by the high nitrogen content, i.e. the formation of EQ grains in IN718N, is due to the formation
of much more TiN particles in the liquid of high [N] alloy. This phenomenon will be further explained by using Hunt’s CET model later in this chapter.

The number of EQ grains increased gradually with the solidification velocity. When the solidification velocity was relatively low, EQ grains appeared first in the center of the castings. No EQ grains were found at the edge of the samples cast in the velocity range of $1.1 \times 10^{-4}\text{ms}^{-1}$ (6.4 mm/min) to $1.7 \times 10^{-4}\text{ms}^{-1}$ (10.0 mm/min) (sample MX201 and MX101) probably due to the highly curved liquidus isotherm. As shown by the solidification simulation (Figure 6-28 to Figure 6-30), the curvature of the liquidus isotherm goes higher with increasing solidification velocity. When the solidification velocity is above $1.1 \times 10^{-4}\text{ms}^{-1}$ (6.4 mm/min), the curvature becomes significant. During the solidification of a complex multi component system such as a superalloy, alloy elements segregate. Solute elements with a distribution coefficient less than 1 are pushed into the liquid at the solidification front. With a flat liquidus isotherm (liquid/solid interface), segregation along the interface is uniform from the center to the edge of ingot. However, more solute could be pushed into the center from the edge when solidifying with a highly curved liquidus isotherm, because in addition to dendrites in the center, edge dendrites could also contribute to the solute segregation at the center, as shown in Figure 7-1. The higher segregated solute content could result in a higher composition undercooling, as described in the literature review chapter of the thesis. Therefore, the nucleation of EQ grains could occur preferentially in the center of the casting. Quantitative analysis of the influence of curvature of isotherm curves on the EQ grain nucleation, however, is beyond the scope of the present project.
With a higher solidification velocity, larger undercooling values are introduced at the solidification front. The undercooling and the change with the increase in solidification velocity has been calculated for alloy IN718 as shown in Table 7-1 and Figure 7-2. The slope of the liquidus, \( m_l \), and the partition coefficients, \( k_i \), for alloy IN718 were taken from the calculation of Boettinger et al. [48]. Refer to Chapter 2 for more details about the calculation procedure and parameters used. Since the composition of IN718PSQ from Canon Muskegon Corp. was slightly different from the composition of normal IN718 from Special Metal Corp., the solidification front undercooling was also calculated for IN718PSQ and the results were shown in Figure 7-2. It can be seen that the composition difference between alloy IN718 and IN718PSQ made a negligible difference in calculating the \( V - AT \) relationship.

When there is a potential nucleation agent such as TiN in the system, as the solidification front undercooling increases, the possibility of nucleation of new grains (EQ grains) becomes larger and consequently more EQ grains appear. When the undercooling is higher than a critical value, a total EQ structure appears and blocks the continuing growth of SX/multi columnar crystals. This critical undercooling is estimated by using Hunt's CET model in the next section. The EQ grain size of the samples cast under high solidification velocities is quite uniform (Figure 6-24, Figure 6-25). Further proving that the EQ grains nucleated on the same inclusion particles, i.e. TiN particles.
7.3 The Breakdown of SX Structure and Calculation of Nucleation Kinetics in Alloy IN718

There are two constants that need to be defined by experiments, the nucleation site density $N_0$ (m$^3$) and the heterogeneous nucleation undercooling at which one site per m$^3$ per second becomes active $\Delta T_N$. Refer to Hunt’s CET model (eq. 2-19 and eq. 2-20). The influence of the variation of $N_0$ and $\Delta T_N$ can be demonstrated in the $V$ vs. $G$ plot. As described in Chapter 2, the undercooling at the solidification front can be calculated by the KGT model for a given solidification rate for a multi-component alloy like IN718. Setting the nucleation site density $N_0 = 1 \times 10^9$ m$^3$, Hunt’s CET model was examined with three different $\Delta T_N$ values: 0.075K, 0.75K and 7.5K, with the results shown in Figure 7-3. It can be seen that with the increase of $\Delta T_N$ value, the CET criteria (for both occurrence of a mixed equiaxed and columnar structure (eq. 2-20) and a breakdown of columnar structure with equiaxed structure (eq. 2-19)) moved to the left of the $V$ vs. $G$ plot at the lower solidification rate. However, in the higher solidification rate range, the CET criteria varied less. The higher the solidification rate, the smaller the change. At the lowest $\Delta T_N$ value (0.075K), Hunt’s CET prediction gave two almost straight lines; the lines curved with the left end moving up when the $\Delta T_N$ value increased. This shows that with the increase of $\Delta T_N$, a CET is increasingly less likely to happen, especially in the lower solidification rate range, which agrees well with the common nucleation theory.

The variation of $N_0$ has a different influence on the change of Hunt’s CET predictions from that of the $\Delta T_N$ value. Three $N_0$ values of $1 \times 10^9$ m$^{-3}$, $0.5 \times 10^9$ m$^{-3}$ and $3.3 \times 10^5$ m$^{-3}$ were
used in Hunt’s CET criteria calculation with a fixed $\Delta T_N = 0.75K$ and the results were shown in Figure 7-4. It can be observed that the two Hunt’s criteria (eq. 2-19 and eq. 2-20) moved to the upper left corner of the $V$-$G$ graph with the decrease of the $N_0$ value. However, unlike changes caused by the varied $\Delta T_N$, the shape of criterion lines did not change, i.e. the lines moved in parallel. This result shows, generally, with an increasing nucleation density $N_0$, the chance for the nucleation of equiaxed grains increases (larger areas in the left of the criterion lines in the $V$-$G$ graph).

The experimental casting results, especially the results of IN718HiN samples, were used to estimate the $N_0$ and $\Delta T_N$ values. Hunt’s CET prediction agreed well with the experimental results, only with a $N_0$ value from about $4.0 \times 10^9 \text{ m}^{-3}$ to about $15.0 \times 10^9 \text{ m}^{-3}$ and a $\Delta T_N$ value from about $2.0 K$ to about $3.1 K$, as shown in Figure 7-5 and Figure 7-6. Any prediction using Hunt’s CET model with a $N_0$ and a $\Delta T_N$ value within the ranges given above agrees well with the experiments, as shown in the example in Figure 7-7. Hunt’s CET model with any $N_0$ and $\Delta T_N$ values outside of the ranges given above will predict a grain structure transition different from the experimental results. Examples of a CET prediction with $N_0$ and $\Delta T_N$ values smaller and larger than the range given above were shown in Figure 7-8 and Figure 7-9 respectively. The liquid temperature gradients at the solid/liquid interface calculated by the ABAQUS thermal model for the samples (Table 6-5) were used in the graphs. A 20% error range was used for the data calculated from ABAQUS.

The average diameter of equiaxed grains in the IN718HiN samples with a columnar-to-equiaxed transition (MX501, MX401 and EX101) was found to be approximately 0.5 cm in
the present experiments, which gives a $N_0$ of about $0.015 \times 10^9 \text{m}^3$, assuming a sphere shape for each equiaxed grain. This number is only 0.1% to 0.4% of the $N_0$ value used in Figure 7-5 and Figure 7-6. The reason for this difference is that Hunt's CET model uses the maximum available number of nucleation sites, but the observed equiaxed grains are those that nucleated and successfully grew later during solidification. As indicated in Chapter 6, the average grain size of the equiaxed grains decreased with the increase of solidification rate. Given the cubic effect in the calculation of volume, a small decrease in grain size represents a large increase of the grain density. Hence with the increase of solidification rate and consequently the increase of solidification front undercooling, the percentage of the nucleation sites that could be activated and actually grow to an equiaxed grain increases.

Similar work to estimate the $N_0$ and $\Delta T_N$ values was carried out for IN718PSQ and normal IN718 samples. However, since there is no equiaxed grain in these samples, there were two possible explanations. First, assuming the same nucleation sites (TiN) exist in normal IN718 as in IN718HiN, the critical nucleation undercooling, $\Delta T_N$, should therefore be the same, i.e. from about 2.0K to about 3.1K. The assumption could be true because normal IN718 contains a nitrogen content close to or higher than the equilibrium nitrogen solubility. In this case, a $N_0$ value of at least $4.5 \times 10^6 \text{m}^{-3}$ or 3000 to 1000 times smaller than the nucleation density in IN718 HiN must be used in order to explain the experimental results, as shown in Figure 7-10. Again, the liquid temperature gradients at the solid/liquid interface calculated by the ABAQUS thermal model for the samples (Table 6-4) were used in the graph. A 20% error range was used for the data calculated from ABAQUS. This analysis shows that even if there are similar nucleation sites such as TiN in the normal IN718 alloy,
the density of these nucleation sites is much lower than that in the IN718HiN alloy.

Second, it could be assumed that there are nucleation sites other than TiN and no TiN exists in the IN718PSQ alloy. The critical nucleation undercooling will therefore be different from the case in which TiN is a nucleation site. In order to have a columnar-to-equiaxed transition with the same nucleation site density \( N_0 = 4.0 \times 10^9 \text{m}^{-3} \) to \( 15.0 \times 10^9 \text{m}^{-3} \), Hunt's CET model has then to apply a critical undercooling of at least 6.3K to fit the experimental results, as shown in Figure 7-11. Once more, the temperature gradients at the solid/liquid interface calculated by the ABAQUS thermal model for the samples (Table 6-3) were used in the graph. A 20% error range was used for the data calculated from ABAQUS. It is worth noting that the 6.3K nucleation undercooling value of IN718 is very close to the critical nucleation undercooling value of 6.7K for other superalloys predicted by other authors such as S. Cockcroft [7] using a different approach. This analysis shows that the addition of large amount of nitride particles (TiN) has dramatically decreased the critical nucleation undercooling in alloy IN718.

The analysis of the equiaxed grain nucleation kinetics of IN718 alloys with three different nitrogen contents was summarized in Table 7-2.

7.4 Spurious Grain Nucleated in the Shroud Corner

As mentioned in Chapter 2, undercooling as high as 40K could occur in the platform/shroud corner during the SX blade/vane casting process. It is interesting therefore to apply the results obtained in section 7.3 to analyze the nucleation of equiaxed grains under
such a high undercooling condition.

If the same nucleation catalysts as TiN particles exist in the solidification front as in normal IN718, or in other words, if $N_0 = 4.5 \times 10^5 \text{m}^{-3}$, $\Delta T_N = 2.5 \text{K}$, the Hunt's model predicts two constant solidification front temperature gradient values $G_1^* = 4.1 \times 10^3 \text{K/m}$ and $G_2^* = 18.9 \times 10^3 \text{K/m}$ as the criteria below which a full breakdown of CX by EQ structure and a mixed structure of CX and EQ occurs respectively. As shown in Figure 7-12, the solidification front temperature gradients of all the IN718PSQ and normal IN718 samples are all below $18.9 \times 10^3 \text{K/m}$, with some of them below $4.1 \times 10^3 \text{K/m}$. In other words, in a shroud corner with 40K solidification front undercooling, if nucleation catalysts like TiN particles exist, even in a very small amount, blades cast under thermal situations similar to those of the present experiments will have spurious grains nucleated, or even a breakdown of the SX structure by the complete EQ structure. Similar calculations may be done for 30K, 20K and 10K undercooling values at the shroud corner, and the critical temperature gradient $G_1^*$ and $G_2^*$ values at different undercooling levels were given in Table 7-3.

If no efficient nucleation catalyst exists, similar to the situation assumed for IN718PSQ in section 7.4, i.e. assuming a critical nucleation undercooling as high as 6.3K under a nucleation site density of $10.0 \times 10^9 \text{m}^3$, Hunt’s model predicts a constant solidification front temperature gradient value, $G_L = 5.3 \times 10^4 \text{K/m}$, as the criterion below which a full breakdown of CX by EQ structure will occur when there is an undercooling value of 40K in the shroud corner. As shown in Figure 7-13, the solidification front temperature gradients of all the IN718PSQ and normal IN718 samples are all below this criterion. In other
words, blades cast under thermal situations similar to those of the present experiments will all have a breakdown of SX structure by equiaxed grains in the shroud corner. Similar calculations have been done for 30K, 20K and 10K undercooling values at the shroud corner, and the critical temperature gradients $G_1^*$ and $G_2^*$ values at different undercooling were given in Table 7-4.

As can be seen from Table 7-3 and Table 7-4, under both nucleation kinetic assumptions, both temperature criteria $G_1^*$ and $G_2^*$ have a linear functional relationship with the shroud corner undercooling, and they decrease quickly with the decrease of shroud corner undercooling. This means that nucleation of spurious grains can be efficiently depressed by either reducing the shroud corner undercooling, or reducing/eliminating nucleation catalysts in the liquid.

7.5 The Sensitivity to Spurious Grains Nucleated from Foreign Particles of IGT SX Superalloys Compared to Alloy IN718

In grain refinement practice for aluminum alloys, the degree of growth restriction for a particular solute is described by the constitutional-supercooling parameter $P$ (eq. 2.29) or the growth-restriction parameter $Q$ (eq. 2.30). For the same effective nucleation catalyst, grain size of alloys with higher $P$ or $Q$ value is easier to be refined. Therefore, the $P$ and $Q$ parameters could be used to evaluate the sensitivity of grain nucleation on a specific foreign particle.

The $P$ and $Q$ values of complex multicomponent systems such as Ni-based superalloys could be calculated by using eq. 2.14. The alloy compositions were taken from Table 2-4. To
simplify the calculation, the slopes of the liquidus, \( m_i \), and the partition coefficients, \( k_i \), of different solute elements of all three kinds of alloys were taken as the same as of IN718, the \( m_i \) and \( k_i \) values of elements that can not be found in IN718 were taken from reference [7]. The \( m_i \) and \( k_i \) values used in the calculation and the calculated pseudo-binary values \( \bar{C} \), \( \bar{m} \), \( \bar{k} \) for alloys were given in Table 7-6 and Table 7-7 respectively.

The calculated \( P \) and \( Q \) values of alloy IN718 and some IGT SX alloys were given in Table 7-5. These values were then normalized by the \( P \) and \( Q \) value of IN718 in order to compare the alloy sensitivity to a foreign inclusion particle such as TiN for spurious grain nucleation. The normalized values \( P' \) and \( Q' \) were shown in Figure 7-14. According to this calculation, 4 of the 6 selected land base SX alloys showed higher tendency to form spurious grains nucleated on TiN particles than alloy IN718, whereas the others showed a slightly lower but similar tendency to IN718.

Since even one spurious grain at a critical location is a rejectable defect in SX castings, the potency of spurious grain nucleation, which is reflected by the constitutional-supercooling parameter \( P \), rather than the restriction of growth of spurious grains reflected by the growth-restriction parameter \( Q \), is the more important factor. It is therefore worth noting that the constitutional-supercooling parameter \( P \) could be more important than the growth-restriction parameter \( Q \) in the evaluation of sensitivity to spurious grains nucleated on inclusion particles of SX superalloys. The IGT SX alloys CMSX-4, PWA1483 and CM186LC showed a much higher tendency to nucleate spurious grains than does IN718, as shown in Figure 7-14. Furthermore, the saturation solubility of TiN in these alloys is usually much
lower than in IN718 (for example, 4 ppm for CMSX4), because of higher content of Ti and other alloying elements. This result reveals the necessity of the extreme restriction on [N] content in these alloys in order to avoid spurious grains.

7.6 Summary

The gap between SX seed and the ceramic mold was found the main cause for the nucleation of secondary columnar grains from the top part of the seed. The chemistry composition of the mold material was eliminated as a source of nucleation. However, the rough surface of ceramic mold was found to have a critical influence on the nucleation of the secondary columnar grains. The growth of secondary columnar grains was analyzed using the concept of the deviation of local normal to the liquid/solid interface curve from the \(<001>\) crystallographic direction, \(\zeta_{2001}\). The inclined \(<001>\) direction of SX seed and the curved \(L/S\) interface were considered important factors influence the competitive growth between grains.

TiN particles were concluded as the nucleation agents for the appearance of EQ grains because EQ grains could only be found in the high nitrogen content samples. The curvature of the solid/liquid interface was used to explain the distribution of EQ grains in the center of samples only with a mid-range solidification speed. Hunt’s CET model was applied to the present experiments, it was found that TiN particles dramatically reduced the critical nucleation undercooling for EQ grain nucleation in IN718 alloys from approximate 6.3K to a range between 2.0K to 3.1K. The calculated nucleation kinetics parameters were then used to analyze spurious grain nucleation in undercooled shroud/platform corners. Reducing the
content of inclusion nucleants such as TiN was found to be an efficient way to depress the formation of spurious grains.

It is interesting to compare mold surface roughness and TiN inclusions as two sources of nucleation of spurious grains. Small secondary grains were usually found on the surface of the ingot cast at a speed in the mid-range or above, when there was enough undercooling in the solidification front, for alloys with all the three [N] levels. They were obviously caused by the defected mold surface. However, these secondary grains were usually separate and long in one direction, so they were identified as columnar crystals. Because these spurious grains originated from the surface, they were rarely found to be able to breakdown the primary crystal structure. Spurious grains caused by nitride inclusions were equiaxed crystals and began to occur when the solidification speed went up to the mid-range or above. They were found in the center of the ingot at lower solidification rates (hence lower solidification front undercooling), and could usually breakdown the primary SX structure when the solidification front undercolling became high enough. Both the rough mold surface and the nitride inclusions are efficient nucleation catalysts for spurious grains, and should therefore be avoided in the SX casting process.

The sensitivity to spurious grains nucleated from foreign particles in IGT SX superalloys was compared with that of alloy IN718 and it was found that most of these SX alloys have the same or higher level of sensitivity in comparison to IN718. Therefore the observation of the influence of TiN particles on the nucleation of spurious grains can be reasonably extended to the SX alloys.
Table 7-1 Solidification Front Undercooling Calculated by the KGT Model for Alloy IN718 at Various Solidification Velocities Used in the Experiments.

<table>
<thead>
<tr>
<th>Solidification velocity x10^{-5} ms^{-1}</th>
<th>Undercooling at solidification front °C</th>
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<tbody>
<tr>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>1.8</td>
<td>1.5</td>
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<tr>
<td>2.5</td>
<td>1.7</td>
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<tr>
<td>3.0</td>
<td>1.9</td>
</tr>
<tr>
<td>3.2</td>
<td>1.9</td>
</tr>
<tr>
<td>3.7</td>
<td>2.0</td>
</tr>
<tr>
<td>4.2</td>
<td>2.2</td>
</tr>
<tr>
<td>4.7</td>
<td>2.3</td>
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<tr>
<td>10.7</td>
<td>3.4</td>
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<td>10.8</td>
<td>3.4</td>
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<td>16.2</td>
<td>4.2</td>
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</tr>
<tr>
<td>25.8</td>
<td>5.2</td>
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<td>27.5</td>
<td>5.3</td>
</tr>
<tr>
<td>34.2</td>
<td>5.9</td>
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</table>

Table 7-2 Summary of Nucleation Kinetics for IN718 Alloys with Different Nitrogen Content.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\Delta T_N$ (K)</th>
<th>$N_0$ (m^{-3})</th>
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</thead>
<tbody>
<tr>
<td>IN718PSQ</td>
<td>&gt; 6.3</td>
<td>(Assumed to be) 4.0x10^9 - 15.0x10^9</td>
</tr>
<tr>
<td>Normal IN718</td>
<td>(Assumed to be) 2.0 - 3.1</td>
<td>&lt; 4.5x10^6</td>
</tr>
<tr>
<td>IN718HiN</td>
<td>2.0 - 3.1</td>
<td>4.0x10^9 - 15.0x10^9</td>
</tr>
</tbody>
</table>
Table 7-3 Hunt's CET Criteria Calculated with $N_0 = 4.5 \times 10^6 \text{m}^{-3}$, $\Delta T_n = 2.5 \text{K}$ for Different Shroud Corner Undercoolings.

<table>
<thead>
<tr>
<th>Shroud undercooling (K)</th>
<th>$G_1^*$ (K/m)</th>
<th>$G_2^*$ (K/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>680.6</td>
<td>3154.7</td>
</tr>
<tr>
<td>10.0</td>
<td>1002.7</td>
<td>4648.0</td>
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<td>20.0</td>
<td>2033.3</td>
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<td>14157.1</td>
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<tr>
<td>40.0</td>
<td>4073.6</td>
<td>18882.4</td>
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Table 7-4 Hunt's CET Criteria Calculated with $N_0 = 10.0 \times 10^9 \text{m}^{-3}$, $\Delta T_n = 6.3 \text{K}$ for Different Shroud Corner Undercoolings.

<table>
<thead>
<tr>
<th>Shroud undercooling (K)</th>
<th>$G_1^*$ (K/m)</th>
<th>$G_2^*$ (K/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>2521.7</td>
<td>11688.7</td>
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<td>30</td>
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<td>40</td>
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<td>245504.4</td>
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Table 7-5 Calculated Constitutional-supercooling Parameter $P$ and the Growth-restriction Parameter $Q$ of Alloy IN718 and Land Base SX Alloys.

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<th>Alloy</th>
<th>Q</th>
<th>P</th>
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<tr>
<td>CMSX-4</td>
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<td>PAW 1483</td>
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<td>SC16</td>
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<td>127.4</td>
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<tr>
<td>RR3000</td>
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<td>95.3</td>
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<tr>
<td>YH61</td>
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<td>69.1</td>
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<tr>
<td>CM 186 LC*</td>
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<td>208.9</td>
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Table 7-6 The Slope of the Liquidus, $m_i$, and the Partition Coefficients, $k_i$ of Different Solute Elements for all Alloys Used in the Present Calculation.

<table>
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<tr>
<th>Elements</th>
<th>$m_i$ (Ref. [20,46])</th>
<th>$k_i$ (Ref. [20,46])</th>
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</thead>
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<td>Co</td>
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<td>Mo</td>
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<td>0.78</td>
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<td>Nb</td>
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<td>Al</td>
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<td>0.64</td>
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<td>Ti</td>
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<tr>
<td>Re</td>
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<td>1.38</td>
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<tr>
<td>W</td>
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<td>1.38</td>
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<td>Ta</td>
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<td>Hf</td>
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<td>-</td>
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<tr>
<td>Fe</td>
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<td>1.16</td>
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</table>
Table 7-7 Calculated Pseudo-binary Values $\bar{C}$, $\bar{m}$, $\bar{k}$ for some Superalloys.

<table>
<thead>
<tr>
<th></th>
<th>IN718</th>
<th>CMSX-4</th>
<th>PWA 1483</th>
<th>SC16</th>
<th>RR3000</th>
<th>YH61</th>
<th>CM 186 LC</th>
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</thead>
<tbody>
<tr>
<td>$C$</td>
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<td>-2.81</td>
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<td>$k$</td>
<td>0.59</td>
<td>0.38</td>
<td>0.36</td>
<td>0.60</td>
<td>0.55</td>
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<td>0.28</td>
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Figure 7-1 A schematic figure showing concave liquidus isotherm and primary dendrites deviated from the vertical growth direction inside the ceramic crucible (the scale is not based on the real dimension).
Figure 7-2 The change of undercooling values with the increase of solidification velocity, calculated for alloy IN718 using the KGT model.
Figure 7-3 The influence of variation of $\Delta T_N$ on the CET prediction of Hunt’s model in alloy IN718 when $N_0 = 1.0 \times 10^9$ m$^{-3}$. Three different $\Delta T_N$ values of 0.075K, 0.75K and 7.5K were used in the calculation.
Figure 7-4 The influence of variation of $N_0$ on the CET prediction of Hunt's model in alloy IN718 when $\Delta T_N = 0.75$K. Three different $N_0$ values of $1.0 \times 10^9$, $0.5 \times 10^9$ and $3.3 \times 10^5$ were used in the calculation.
Figure 7-5 The grain structure of all IN718HiN samples and Hunt's CET model best fitting the casting results with a minimum value of $N_0 = 4.0 \times 10^9 \text{m}^{-3}$ and $\Delta T_a = 2.0 \text{K}$.
**Figure 7-6** The grain structure of all IN718HiN samples and Hunt's CET model best fitting the casting results with a maximum value of $N_0 = 15.0 \times 10^9 \text{ m}^{-3}$ and $\Delta T_n = 3.1 \text{K}$. 
Figure 7-7 The grain structure of all IN718HiN samples and Hunt’s CET model prediction with \( N_0 = 7.0 \times 10^9 \text{m}^{-3} \) and \( \Delta T_s = 2.5 \text{K} \).
Figure 7-8 The grain structure of all IN718H1N samples and Hunt’s CET model prediction with $N_e = 3.8 \times 10^6 \text{ m}^{-3}$ and $\Delta T_s = 0.75 \text{K}$.
Figure 7-9 The grain structure of all IN718HiN samples and Hunt's CET model prediction with $N_0 = 40.0 \times 10^9 \, \text{m}^{-3}$ and $\Delta T_n = 3.7 \, \text{K}$.
Figure 7-10 The grain structure of all normal IN718 samples and Hunt’s CET model best fitting the casting results with $\Delta T_s = 2.0K$ and $3.1K$ and a nucleation site density $N_0 = 4.5 \times 10^6 \text{ m}^{-3}$. 
**Figure 7-11** The grain structure of all normal IN718PSQ samples and Hunt's CET model best fitting the casting results with nucleation site density $N_0 = 4.0 \times 10^6 \text{m}^{-3}$ and $15.0 \times 10^7 \text{m}^{-3}$ and a critical nucleation undercooling $\Delta T_n = 6.3 \text{K}$.
Figure 7-12 Applying Hunt’s model in shroud/platform corner with 40K solidification front undercooling to alloy with nucleation catalysts similar to TiN but with even a much less density gives two constant $G_L$ values as CET criteria, which are in or above the $G_L$ range of the present experiment.
Figure 7-13 Applying Hunt’s model in shroud/platform corner with 40K solidification front undercooling to alloy with nucleation catalysts different from TiN particles and with even a much less density gives a constant $G_L$ value as CET criterion, which are much above the $G_L$ range of the present experiment.
Figure 7-14 Normalized constitutional-supercooling parameter $P'$ and growth-restriction parameter $Q'$ of IN718 and various land base SX alloys.
Chapter 8 Conclusions and Recommendations for Further Work

8.1 Conclusions

1. Cylindrical SX ingots were cast in a Bridgman furnace for three IN718 alloys with nitrogen content lower than (less than 10 PPM, IN718PSQ), close to (about 47 PPM, normal IN718) and higher than (about 86 PPM, IN718N) the nitrogen saturation solubility at the liquidus (39 PPM) respectively using the seed method. The oxygen content of all the alloys was controlled to eliminate the influence of oxide inclusions on the solidification behavior of ingots;

2. Except for samples with normal nitrogen content at low solidification velocities, which were cast with 1733K (1460°C) hot zone temperature, all samples were cast with 1773K (1500°C) hot zone temperature;

3. The solidification velocity was changed from $1.5 \times 10^{-5} \text{ ms}^{-1}$ (0.9 mm/min) to $3.4 \times 10^{-4} \text{ ms}^{-1}$ (20.5 mm/min) for each alloy in order to vary the undercooling at the solidification front;

4. No equiaxed grain was found in ingots of IN718 with low (IN718PSQ) and normal nitrogen levels in the solidification velocity range;

5. Equiaxed grains occurrence increased in the ingot gradually with the increase of solidification velocity. The columnar to equiaxed transition was observed in samples of
IN718 with high nitrogen content cast at solidification velocity equal to or higher than $2.1 \times 10^{-4} \text{ms}^{-1}$ (12.5 mm/min);

6. TiN inclusions were considered to be a good nucleation catalyst of spurious grains in a SX ingot of alloy IN718. They were estimated to reduce the critical nucleation undercooling for the nucleation of equiaxed grains from about 6.3K to a range from 2.0K to 3.1K in alloy IN718;

7. IGT SX alloys were estimated with a tendency to nucleate spurious grains on inclusion particles which is either close to or higher than the tendency of alloy IN718, by comparing constitutional-supercooling parameter $P$ and growth-restriction parameter $Q$;

8. A 2D thermal model of the SX casting process was built using commercial FE software ABAQUS;

9. The solidification interface was found to become more concave when the solidification velocity increases;

10. Other solidification defects such as large or small columnar crystals occurred in most of the ingots, especially those solidified at high velocity. The nucleation of these defects was analyzed and found to be related to the seed defects, the solidification interface curve and the mould internal surface condition especially the surface of the ceramic plug made of alumina cement.
11. Nucleation kinetics calculation showed that normal IN718 could contain TiN inclusions as nucleation catalyst, however in a considerably lower density than in IN718N;

12. It was estimated by theoretical analysis that eliminating TiN particles would be an efficient way to avoid spurious grains in an undercooled platform/shroud corner of IGT SX blade/vane castings.

8.2 Recommendations for Further Work

1. To cast IN718PSQ and normal IN718 ingots at solidification velocity higher than $3.4 \times 10^{-4}$ ms$^{-1}$ (20.5 mm/min) and validate the nucleation kinetics calculated for IN718PSQ and normal IN718;

2. To cast more IN718 alloy with different nitrogen content at the normal solidification velocity used in the industry and hence find the critical nitrogen content above which a CET would occur in the normal industrial solidification range (temperature gradient and withdrawal speed);

3. To find the aforementioned critical nitrogen contents for undercooling values typically observed at the shroud corner of industrial SX blades/vanes for alloy IN718;

4. To extend the current experiments of IN718 to industrial SX alloys;

5. To analyze the crystallographic relations between the spurious grains and the TiN particles on which they are nucleated;
6. To test the influence of other inclusions like HfN and oxides on the nucleation of spurious grains;

7. To suggest modifications on alloy specifications, in terms of nitrogen and oxygen contents, based on experiments and analysis.
Reference


87. X. Huang, Y. Zhang, Z. Hu and Y. Liu: “Thermodynamics of Inclusion Formation in a Ni-Based Superalloys”.


96. A. Mitchell: *Chemical Problems in EB melting*.

97. A. Mitchell: *Thermochemistry of Inclusions in Superalloys*.


106. ABAQUS, Users Manuals, Version 6.2, developed by HKS, Pawtucket, RI, USA.
Appendix A: ABAQUS input file

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  287,
  288
*ELSET, ELSET=CT_FS_1, GENERATE
  286,
  288
*ELSET, ELSET=CT_MD
  409,
  417,
  425,
  433,
  441,
  449,
  457,
  465,
*ELSET, ELSET=CT_MD_1
  281,  289,  297,  305,  313,  321,  329,  337,
  345,  353,  361,  369,  377,  385,  393,  401
*ELSET, ELSET=CT_SP
  514,  515
*ELSET, ELSET=SP_CT
  547,  551
*ELSET, ELSET=SP_MD, GENERATE
  520,  523,  1
*ELSET, ELSET=SP_MD_1
  523,  527,  531,  535,  539,  543
*ELSET, ELSET=SP_CL
  520,  524,  528,  532,  536,  540
*ELSET, ELSET=SP_CL_1
  544,  548
*ELSET, ELSET=BAF
  583,  584
*ELSET, ELSET=BAF_1, GENERATE
  583,  583,  1
  585,  604,  1
*ELSET, ELSET=BAF_2
  583,
*ELSET, ELSET=CHA, GENERATE
  616,  626,  1
  628,  647,  1
  649,  658,  1
*ELSET, ELSET=CHA_1, GENERATE
  606,  616,  1
*ELSET, ELSET=SUS, GENERATE
  578,  582,  1
*ELSET, ELSET=SUS_1, GENERATE
  552,  576,  1
*ELSET, ELSET=CL_FS
  6,   12,  18,  24,  27,  30,  33,  36,
  39,  42,  45,  48,  51,  54,  57
*ELSET, ELSET=CL_FS_1, GENERATE
  1,   3,   1
*ELSET, ELSET=CL_FS_2
  1,   4,   7,  10,  13,  16,  19,  22,
  25,
** pp1_cl
**
*SURFACE, TYPE=ELEMENT, NAME=spp1_cl
PP1_CL, S4,
** pp2_cl
**
*SURFACE, TYPE=ELEMENT, NAME=spp2_cl
PP2_CL, S4,
** pp3_cl
**
*SURFACE, TYPE=ELEMENT, NAME=spp3_cl
PP3_CL, S4,
** pp4_cl
**
*SURFACE, TYPE=ELEMENT, NAME=spp4_cl
PP4_CL, S4,
** cl_pp1
** SURFACE, TYPE=ELEMENT, NAME=scl_pp1
CL_PP1, S2,
**
** cl_pp2
**
** SURFACE, TYPE=ELEMENT, NAME=scl_pp2
CL_PP2, S2,
**
** cl_pp3
**
** SURFACE, TYPE=ELEMENT, NAME=scl_pp3
CL_PP3, S2,
**
** cl_pp4
**
** SURFACE, TYPE=ELEMENT, NAME=scl_sp
CL_SP, S4,
**
** cl_md
**
** SURFACE, TYPE=ELEMENT, NAME=smd_cl
MD_CL, S1,
**
** md_sp
**
** SURFACE, TYPE=ELEMENT, NAME=smd_sp
MD_SP_1, S4,
MD_SP, S2,
**
** md_ct
**
** SURFACE, TYPE=ELEMENT, NAME=smd_ct
MD_CT, S1, 1.
MD_CT_1, S2, 1.
**
** ct_md
**
** SURFACE, TYPE=ELEMENT, NAME=sct_md
CT_MD_1, S3, 1.
CT_MD, S2, 1.
**
** ct_sp
**
** SURFACE, TYPE=ELEMENT, NAME=sct_sp
CT_SP, S1, 1.
**
** sp_ct
**
** SURFACE, TYPE=ELEMENT, NAME=ssp_ct
SP_CT, S4, 1.
**
** sp_md
**
**SURFACE, TYPE=ELEMENT, NAME=ssp_md
SP_MD, S2, 1.
SP_MD_1, S3, 1.
**
** sp_cl
**
**SURFACE, TYPE=ELEMENT, NAME=ssp_cl
SP_CL, S1, 1.
SP_CL_1, S2, 1.
**
**
**define contact pairs and heat transfer coefficient
**
**
*CONTACT PAIR, INTERACTION=in_ct_md
sct_md, smd_ct
*SURFACE INTERACTION, NAME=in_ct_md
*GAP CONDUCTANCE
5.0, 0., 20.
5.0, 0.01, 20.
100.0, 0., 600.
100.0, 0.01, 600.
180.0, 0., 800.
180.0, 0.01, 800.
200.0, 0., 924.
200.0, 0.01, 924.
700.0, 0., 1260.
700.0, 0.01, 1260.
1000.0, 0., 1336.
1000.0, 0.01, 1336.
9480.0, 0., 2000.
9480.0, 0.01, 2000.
**
*CONTACT PAIR, INTERACTION=in_ct_sp
sct_sp, ssp_ct
*SURFACE INTERACTION, NAME=in_ct_sp
*GAP CONDUCTANCE
300.0, 0.
300.0, 0.01
**
*CONTACT PAIR, INTERACTION=in_sp_md
ssp_md, smd_sp
*SURFACE INTERACTION, NAME=in_sp_md
*GAP CONDUCTANCE
250.0, 0.
250.0, 0.01
**
*CONTACT PAIR, INTERACTION=in_sp_cl
ssp_cl, scl_sp
*SURFACE INTERACTION, NAME=in_sp_cl
*GAP CONDUCTANCE
400.0, 0.
400.0, 0.01
**
*CONTACT PAIR, INTERACTION=in_cl_md
scl_md, smd_cl
*SURFACE INTERACTION, NAME=in_cl_md
*GAP CONDUCTANCE
200.0, 0.
200.0, 0.01
**
*CONTACT PAIR, INTERACTION=in_cl_pp
scl_pp1, sppl_cl
*CONTACT PAIR, INTERACTION=in_cl_pp

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scl_pp2, spp2_cl
*CONTACT PAIR, INTERACTION=in_cl_pp
scl_pp3, spp3_cl
*CONTACT PAIR, INTERACTION=in_cl_pp
scl_pp4, spp4_cl
*SURFACE INTERACTION, NAME=in_cl_pp
*GAP CONDUCTANCE
4500.0, 0
4500.0, 0.01
**
**
** define exposed surface
**
** pp4_fs
**
*SURFACE, TYPE=ELEMENT, NAME=spp4_fs, PROPERTY=pscu
PP4_FS, S1,
PP4_FS_1, S2,
PP4_FS_2, S3,
**
** pp3_fs
**
*SURFACE, TYPE=ELEMENT, NAME=spp3_fs, PROPERTY=pscu
PP3_FS, S1,
PP3_FS_1, S2,
PP3_FS_2, S3,
**
** pp2_fs
**
*SURFACE, TYPE=ELEMENT, NAME=spp2_fs, PROPERTY=pscu
PP2_FS, S1,
PP2_FS_1, S2,
PP2_FS_2, S3,
**
** pp1_fs
**
*SURFACE, TYPE=ELEMENT, NAME=spp1_fs, PROPERTY=pscu
PP1_FS, S1,
PP1_FS_1, S2,
PP1_FS_2, S3,
**
** md_fs
**
*SURFACE, TYPE=ELEMENT, NAME=smd_fs, PROPERTY=psmd_fs
MD_FS_1, S2,
MD_FS_2, S3,
MD_FS, S1,
MD_FS_3, S4,
**
** ct_fs
**
*SURFACE, TYPE=ELEMENT, NAME=sct_fs, PROPERTY=psct_fs
CT_FS_1, S4,
CT_FS, S3,
**
** baf
**
*SURFACE, TYPE=ELEMENT, NAME=sbaf, PROPERTY=pscu
Baf, S1,
Baf_1, S2,
Baf_2, S4,
**
** cha

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**
*SURFACE, TYPE=ELEMENT, NAME=scha, PROPERTY=pscha
CHA_1, S4,
CHA, S1,
**
** sus
**
*SURFACE, TYPE=ELEMENT, NAME=ssus, PROPERTY=pssus
SUS_1, S3,
SUS, S2,
**
** cl_fs
**
*SURFACE, TYPE=ELEMENT, NAME=ycll, PROPERTY=pscu
CL_FS_1, S3,
CL_FS_2, S4,
CL_FS, S2,
**
**
**define surface emissivity
**
**
*SURFACE PROPERTY, NAME=psct_fs
*EMISSIVITY
0.9,
**
*SURFACE PROPERTY, NAME=psmd_fs
*EMISSIVITY
0.9,
**
*SURFACE PROPERTY, NAME=pscu
*EMISSIVITY
0.3,
**
*SURFACE PROPERTY, NAME=pssus
*EMISSIVITY
0.9,
**
*SURFACE PROPERTY, NAME=pscha
*EMISSIVITY
0.4,
**
**
** define cavity
**
**
*CAVITY DEFINITION, NAME=blue_box
sct_fs, smd_fs, scl_fs, spp1_fs, spp2_fs, spp3_fs, spp4_fs, ssus, sbaf, scha
**
**
** INI_ca_md
**
*INITIAL CONDITIONS, TYPE=TEMPERATURE
INI_CA_M, 1250.
**
** INI_spa
**
*INITIAL CONDITIONS, TYPE=TEMPERATURE
INI_SPA, 600.
**
** INI_ch
**
*INITIAL CONDITIONS, TYPE=TEMPERATURE
INI_CH, 15.
**
**
*INITIAL CONDITIONS, TYPE=FIELD
PSET2, 0.0
**
**********************************************************************************************************************
** Step 1, melting ingot
** LoadCase, Default
**
*STEP, INC=10000, UNSYM=YES
*HEAT TRANSFER, END=SS, DELTMX=10.
  0.001, 1700., 0.000001, 5., 0.005
*RADIATION VIEWFACTOR, CAVITY=blue_box, VTOL=0.05
**
*NSET, NSET=T_PIPE
  640, 642, 644, 646, 648, 650, 652, 654
*NSET, NSET=PSET7, GENERATE
  812, 919, 1
*NSET, NSET=BAF_1, GENERATE
  767, 769, 2
  770, 807, 1
  808, 810, 2
*NSET, NSET=SUS_1, GENERATE
  716, 763, 1
*NSET, NSET=PSET2, GENERATE
  360, 638, 1
*NSET, NSET=INI_CA_M, GENERATE
  81, 638, 1
*NSET, NSET=INI_SPA, GENERATE
  655, 699, 1
*NSET, NSET=INI_CH, GENERATE
  1, 80, 1
  639, 639, 1
  641, 641, 1
  643, 643, 1
  645, 645, 1
  647, 647, 1
  649, 649, 1
  651, 651, 1
  653, 653, 1
**
**
** Fixed Temperature of Chill PTypes
**
*BOUNDARY, OP=NEW
T_PIPE, 11, 11, 15.
**
** Fixed Temperature of Chamber
**
*BOUNDARY, OP=NEW
PSET7, 11, 11, 15.
**
** Fixed Temperature of Baffle
**
*BOUNDARY, OP=NEW
  764, 11, 11, 100.
  765, 11, 11, 100.
  766, 11, 11, 800.
  768, 11, 11, 800.
  BAF_1, 11, 11, 100.
**
** Fixed Temperature of Susceptor
**
*BOUNDARY, OP=NEW

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** Step 2, directional solidification
** LoadCase, Default
**
*STEP, INC=10000, UNSYMM=YES  
*HEAT TRANSFER, END=PERIOD, DELTMX=10.  
  0.001,  2500.,  0.00000001, 0.5
*RADIATION VIEWFACTOR, CAVITY=blue_box, VTOL=0.05, NSET=ENCLOSUR, MDISP=0.001  
*AMPLITUDE, NAME=speed  
  0., 0., 10000., 0.55  
*MOTION, TRANSLATION, TYPE=DISPLACEMENT, AMPLITUDE=speed  
  ENCLOSUR, 2, 2, 1  
*END STEP
Appendix B: user subroutine tao_grad.f

SUBROUTINE USDFLD(FIELD, STATEV, PNEWDT, DIRECT, T, CEBENT,
1 TIME, DTIME, CMNAME, ORNAME, NFIEL, STATV, NOEL, NPT, LAYER,
2 KSTEP, KINC, NDI, NSHR, COORD, JM, JMATYP, MLAYO,
3 LACCLA)

C INCLUDE 'ABA_PARAM.INC'

C CHARACTER*80 CMNAME, ORNAME
CHARACTER*8 FLGRAY(15)
DIMENSION FIELD(NFIELD), STATEV(NSTATV), DIRECT(3,3),
1 T(3,3), TIME(2)
DIMENSION ARRAY(15), JARRAY(15), JM(*) , JMATYP(*), COORD(*)
DIMENSION G(4)
OPEN(UNIT=15, FILE="/vhe/hp99/users/h98709/ALS01/output.dat",
& status='unknown', access='append', form='formatted')

C Calculate the gradient at each material integration point.
C
C Call GETVRM to retrieve the current temperature
CALL GETVRM('TEMP', ARRAY, JARRAY, FLGRAY, JRCD, JM, JMATYP,
1 MLAYO, LACCLA)
TEMP = ARRAY(1)
IF ((TEMP.LT.1337D0).AND.(TEMP.GT.133SD0))THEN
    C The heat flux vector in the element must be retrieved using
    GETVRM.
    C
    CALL GETVRM('HFL', ARRAY, JARRAY, FLGRAY, JRCD, JM, JMATYP,
1 MLAYO, LACCLA)
    C
    WRITE(7,*) NOEL, 'Temp', TEMP, 'HFL', ARRAY(1)
    COND = 26.0
    C calculate cooling rate
    C CLGRT = (TEMP-STATEV(5))/DTIME
    C Divide the HFL vector by the -conductivity to get the thermal
    C gradient. The first value in HFL is the magnitude and the second,
    C third and forth values are the individual components.
    DO I=1, 4
        G(I) = ARRAY(I) / COND
        STATEV(I) = G(I)
    ENDDO
    C VLC = CLGRT/G(1)
    IF (COORD(1).LT.0.001) THEN
        WRITE(15,99) COORD(1), TIME(2), COORD(2), G(1), TEMP
    ENDF
99 FORMAT(E12.5, 5(IX, E12.5))

STATEV(5) = TEMP
Close (unit=15)