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Preventing solidification defects in large superalloy castings used in advanced electric power systems

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**Preventing Solidification Defects in Large Superalloy Castings Used in Advanced
Electric Power Systems**

Jairo Antonio Valdés Ortiz

**Dissertation submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
In
Mechanical Engineering**

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Number Criterion**

ABSTRACT

Preventing Solidification Defects in Large Superalloy Castings Used in Advanced Electric Power Systems

Jairo A. Valdés Ortíz

The need for clean and affordable power has resulted in great demand for high-efficiency gas turbine power systems. To improve energy generation efficiency, and lower CO₂ emissions, the new generation of land based gas turbines needs to be larger and operated at a higher temperature. Consequently, it is required the use of Nb-containing superalloys such as Inconel 718 for the rotor disk, to avoid overaging of the microstructure during the forging process, but its applicability is being limited by difficulties in the reliable production of large Vacuum Arc Remelting (VAR) ingots (33 to ~35 in. diameter) without macrosegregation defects such as freckles and center segregation. These defects impair the mechanical properties of the material and are believed to be caused by convection in the mush layer. Because they cannot be corrected by subsequent treatment, the affected ingots should be scrapped highly increasing the production costs.

In this work, the aim was to take steps toward the final goal of preventing macrosegregation defects in VAR ingots by assessing the need for accurate determination of the driving force related to the solutal buoyancy in the mushy layer and postulating a criterion for freckling prediction that could better resolve if freckles will or will not evolve under certain processing conditions. An experimental methodology was proposed to determine the partition coefficients of the major solute elements and better agreement was obtained with the predictions made with the newly developed databases, suggesting that improvements in the accuracy of the theoretical predictions can still be obtained and are necessary for freckling prediction. Quenching modified DTA (MDTA) tests were proven to be suited for measuring the partition coefficients of the solute elements, and it was assumed successfully that the cooling rate prior to the quenching step of 0.083 Ks⁻¹ was slow enough to permit easy quenching, while being sufficiently fast for the primary solidification reaction to depart from the equilibrium model and being closer to the Scheil model. The minimization of the error function defined from the Scheil equation was found to be an appropriate method for describing the segregation profiles of the quenched samples and permitted good estimations of the partition coefficients of the solute elements. A criterion for freckling prediction that includes the effect of tilted solidification front was proposed. The form includes the effect of the tilt angle by preserving the anisotropic nature of the permeability tensor throughout the derivation and uses Poirier's experimentally determined functional forms for the parallel and perpendicular components. The proposed form of Rayleigh number criterion was found to provide better resolution when evaluated against available experimental data in the literature. Especially, it showed that the nucleation of channels in the mushy layer leading to freckles is equally probable in the proximity of the tips of the dendrites or deeper in the mushy layer, for example at approximately 0.7 liquid fraction and 0.4 liquid fraction respectively, depending on the angle of tilt of the solidification front.

To my beloved Family

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1. INTRODUCTION

1.1 Scope of This Work

With the growing need of improving the efficient use of fossil fuels while reducing the environmental impact, electric power generation technology is facing great challenges. During the last decade, the U.S. Department of Energy has been taking steps in that direction by developing research through cooperation involving Industry, Universities, and National Laboratories.¹ One example of the many envisioned methodologies conceives research in technological modules, that can be assembled together and design power plants for site/region specific markets. It is aimed to design flexible plants, that can be fueled with coal, natural gas, biomass, petroleum coke (from oil refineries), and municipal waste. Assuming the implementation of Carbon sequestration, a goal of zero emissions is proposed in concord with achievement of higher efficiencies: in excess of 60 % for Coal-fueled, and over 75 % for Gas-fueled. These higher efficiencies not only will result in lower operation costs in electric power production, but also will allow a greatly important concomitant decrease of green house gas emissions to be managed.

To fulfill these goals it is required to continue research advancements on materials and process development. Progress in manufacture processing and materials used in the hot section parts of gas turbines have contributed to obtain an increment of the combined cycle efficiency over five percentage points during the last three decades^{2, 3}. Further improvements of efficiency are expected by increasing the firing temperature and the size of the gas turbines⁴. The large VAR superalloy ingots required to produce the rotor discs for the new generation of gas turbines, and to satisfy the demand of these materials in power applications (e.g. advanced ultra super critical steam turbines), require the use of materials with improved resistance to over-aging during the hot working process of the massive parts⁵. The material of choice is the alloy 718, which is strengthened by Nb additions and has been used for decades in the aeronautics industry for fabrication of rotors in aircraft engines. Unfortunately, the improvements in the creep resistance obtained by alloy 718 have a concomitant decrease of castability, and the large ingots have high propensity of developing solidification defects like center segregation, white spots, and channel segregates like freckles. These problems limit alloy 718 applicability to 33~35 in. diameter ingots⁶.

In particular, channel segregates like freckles are highly detrimental. They consist of discontinuities where the material solidifies as equiaxed grains with a composition high on alloy elements, elevated percentage of eutectic phases and shrinkage porosity. Because they constitute crack initiation sites that cannot be corrected during the subsequent thermo-mechanical treatment and impair the mechanical properties, affected ingots should be scrapped increasing the production costs. Freckles are also a main cause of rejection in single crystal manufacture process of superalloy parts, such as gas turbine blades. Freckles and misoriented columnar grains are unwanted breakdowns of the single crystal solidification which have been found to be linked with convective instabilities.⁷ Better understanding and greater body of experimental data about the freckle formation

mechanism in VAR ingots are pursued to make more accurate predictions and propose strategies to prevent their formation.

Improved control of the process and rigorous quality assurance of electrodes in the VAR process have contributed to reduce the incidence of freckles in large superalloy ingots,⁸ but freckles are still found, especially when the VAR process stability is perturbed by transients which may not be completely characterized.^{9,10} Concurrent engineering efforts are believed to be necessary in the task of expanding the processing window of large VAR ingots and designing new compositions for superalloy castings.¹¹

Accurate predictive capacity and comprehensive understanding of nucleation and growth of freckles are needed. Furthermore, it is important to realize that most of the macrosegregation defects in castings are associated to a common origin. The desirable advances toward understanding of transport phenomena and freckle formation in VAR ingots should be also useful in preventing other frequently found patterns like center segregation.

In 2004, researchers in WVU lead a cooperative research effort within the conception of the State Technologies Advancement Collaborative initiative by the U.S Department of Energy, including partnership with Penn State University, Special Metals Corporation (SMC) and GE.¹² This project gave continuity to research work previously developed between WVU and SMC scientists on the compositional effects on the macroscopic evolution of freckles and the development of a freckling criterion.^{13, 14} To great extend, the 2004 project motivated and supported the research efforts presented here.

1.2 Objectives

The main objectives proposed in this research were the following:

- (i) Systematically investigate the partition coefficients of the major alloying elements in Ni-base superalloys I-706 and I-718 (Nb, Al, Ti) through experimental verification with support of thermodynamic calculation.
- (ii) Set up solidification model by coupling the outcomes from (1) and the previous developed model at WVU and verify it by horizontal directional solidification tests.
- (iii) Provide the guideline of composition and processing control to minimize the solidification macrosegregation for the superalloy producer.

1.3 Outline of This Thesis

Chapter two corresponds to the literature review. The most relevant publications with a direct relation to the objectives are summarized. Chapter three presents the methodology followed, and its main purpose is to provide a conceptual map for the general methods and assumptions used, and their impact over the outcomes from this research work. However, for clarity and completeness some relevant methodological details are also

included in the corresponding chapters when it was required. Chapter four includes the most important results obtained in the determination of the partition coefficients of the solute elements on Ni-base simplified superalloys by experimental approach with verification by thermodynamic calculations. Chapter five briefly summarizes the development of an original formulation proposed for a freckling criterion that constitutes a contribution that provides a tool for theoretical prediction of freckles formation in Ni-based superalloy VAR Ingots. Chapter six includes an evaluation of the prediction capabilities of the proposed freckling criterion using available experimental data. Chapter seven summarizes the important conclusions reached in this research and includes the future work.

The material presented in this document has been published in the following conferences and peer reviewed journals:

Conference articles:

Jairo Valdes, Xingbo Liu, Shun-Li Shang, Zi-Kui Liu: *Partition Behavior of Nb in the Ni-Cr-Fe-Nb Alloy System*, AEROMAT 18th Conference and Exposition 2007, ASTM, Baltimore, Maryland USA.

Jairo Valdes, DongEung Kim, Shun-Li Shang, Xingbo Liu, Paul King, Zi-Kui Liu: *Investigation of the Partition Coefficients in the Ni-Fe-Nb Alloys: A Thermodynamic and Experimental Approach*, Superalloys, TMS (The Minerals and Materials Society), Champion PA, 2008, pp. 333-337

Jairo Valdes, Xingbo Liu, Paul King, Christopher Cowen, Paul Jablonski: *Solidification Front Tilt Angle Effect on Potential Nucleation Sites for Freckling in the Remelt of Ni-Base Superalloys*, 7th International Symposium on Superalloy 718 and Derivatives 2010, TMS (The Minerals and Materials Society) – Accepted

Journal papers:

Jairo Valdes, Shun-Li Shang, Zi-Kui Liu, Paul King, Xingbo Liu: *Quenching Differential Thermal Analysis and Thermodynamic Calculation to Determine Partition Coefficients of Solute Elements in Simplified Ni-Base Superalloys*, Metallurgical and Materials Transactions A, vol. 41A, pp. 487- 498

Jairo Valdés, Paul King and Xingbo Liu: *On the formulation of a Freckling Criterion for Ni-Based Superalloy Vacuum Arc Remelting Ingots*, Metallurgical and Materials Transactions A, vol. 41, pp. 2408-2416.

2. LITERATURE REVIEW

The problem of macrosegregation in castings has been recognized for centuries. It has been reported one of the first technical publications treating the macrosegregation of bronze in the manufacture of gun barrels authored by Vannoccio Biringuccio in 1540. Because macrosegregation during solidification involves various physical phenomena, it is a dynamical research field attractive to many disciplines including mechanical engineering, materials science, applied mathematics, astro/geophysics, etc. Consequently, there is a vast literature related to macrosegregation and this review only includes the most relevant publications with regard to the objectives proposed.

2.1 Manufacture Processing of Rotor Discs for Land Based Gas Turbines

The manufacture process of gas turbine rotor discs by conventional ingot metallurgy usually includes at least six different steps that are designed to efficiently modify the chemical composition and microstructure. The final material properties must provide exceptional integrity for extreme operational conditions. Basically the rotor discs require, like most critical rotary machine elements, high tensile strength, high ultimate strength, excellent fatigue resistance and fracture toughness; but with the paramount condition that all of these properties must be maintained for long periods of time, while exposed to high temperatures nearing 0.75 times their melting point. Hence, additionally to the mentioned properties, they should have outstanding creep resistance, dimensional stability and corrosion resistance at elevated temperatures. To meet all requirements, the chemical composition of superalloys used generally contains more than 13 different elements between tuned additions and controlled impurities¹⁵. Furthermore, the final alloying elements distribution (in solid solution or in precipitated secondary phases), the grain size distribution and the residual stresses state need to be optimized, and this results in processing steps with closely controlled parameters within narrow variation ranges (so-called small processing window). Fig. 2.1 presents a flow diagram of the typical manufacture route.

Fig. 2.1 Manufacture route for rotor discs of gas turbines.

Commonly, the manufacture process starts with a stage of Vacuum Induction Melting (VIM) to produce an electrode free of contaminant elements. In the VIM stage about 30

elements are refined from the superalloy stock, including critical elements like Oxygen, Nitrogen, Carbon, Sulfur, and low melting point metals introduced with the recycled material.¹⁶ The obtained electrode with a refined composition is then remelted in secondary steps of Electro Slag Remelting (ESR) and Vacuum Arc Remelting (VAR). The ERS/VAR steps are intended to adjust the chemistry of the alloy but more importantly, to provide a sound ingot, with homogeneous macrostructure and free of solidification defects. Next, the as-cast VAR ingots are subject to a homogenization heat treatment to dissolve the precipitated eutectic phases, decrease the uneven distribution of alloying elements within the dendrites (microsegregation coring) and refine the grain size to optimize the microstructure for hot working. The following hot working steps are composed of cogging the ingots to billets with the appropriate size and shape, while providing grain refinement by recrystallization of the plastically deformed material. The near shape billets are forged to pre-shaped discs that consequently receive a final heat treatment. This heat treatment usually is accomplished by two steps. The primary step consists of solution annealing followed by quenching and aging (precipitation hardening). The secondary step usually is a lower temperature aging that reduces the residual thermal stresses, which is crucial in order to adhere to the tight tolerances required in the final shape after machining. Also, the secondary aging has the objective of stabilizing the secondary phase precipitates. The last step of manufacture consists of machining to the final dimensions within the tolerances. Certainly, there are many different configurations for the production of discs by ingot metallurgy approach, some of which aim to decrease the incidence of macrosegregation defects for large size ingots by including more remelting steps¹⁷.

Tin *et al.*¹⁸ presented results on integrated modeling manufacture approach by combining computational models proposed through the years for the individual stages of secondary remelting, hot working, and final heat treatment, and obtained predictions of microstructure evolution. By assuming the presence of macrosegregation defects, the material points were traced through the processing and concluded, as empirically known through industrial practice, that segregation patterns like freckles located at the midradius of the ingot could not be eliminated by machining from the final shape and prevention was the only available solution to avoid their presence on the finished part.

2.2 Macrosegregation Defects in Castings

The term macrosegregation is used to describe the non homogeneous distribution of the alloying elements in a casting. Regularly, macrosegregation patterns extend over distances that range from millimeters to several centimeters and are characterized for having a local solute content that is higher (positive segregation) or lower (negative segregation) than the nominal composition of the alloy. As the chemical composition influences the microstructure and thus the properties of the material, the macrosegregation impairs the response to the operational requirements.

It has passed more than four decades since it was first recognized that virtually all the macrosegregation patterns could be linked to a common origin, lying on interactions between the solidifying metal and flow of the remaining liquid. At the vicinity of the

advancing liquid-solid interface, the liquid typically has a chemical composition enriched in solute elements due to the decreased solubility of the alloying additions in the solid with respect to the liquid phase (microsegregation). Because of numerous causes associated to the physical phenomena and processing conditions, the segregated liquid in the microscale is transported over long distances. The interdendritic liquid flow could fracture, erode and remelt crystals of already formed solid, producing discontinuities and the lack of chemical homogeneity observed in the macroscale. It could be driven by solidification/thermal contractions (shrinkage), natural convection, and external influences, which in turn are dependent on the heat transfer, buoyancy, liquid metal properties, and electromagnetic Lorentz forces from the arc processing dynamics. At the end of solidification, the macrostructure might exhibit a combination of patterns including center segregation, A-segregates, V-segregates, white spots, tree rings and freckles. Differently to microsegregation, which occurs in small scale distances and can be corrected by the use of engineered heat treatment processes¹⁹, macrosegregation patterns are practically impossible to eliminate because they require correcting actions that are economically or technically prohibitive. Figure 2.2 depicts some examples of macrosegregation geometrical distributions that could be found within an ingot. The symbols (+) and (-) correspond to locations where the alloying elements content is higher or lower than the nominal composition respectively.

Fig. 2.2 Typical macrosegregation patterns in steel ingots

Depending on the context, freckles, V-segregates and A-segregates are frequently referred with exchanged names since they have similar chemistry and share microscopic morphological characteristics²⁰. Regardless of the name given, freckles are channel segregates that are critical and it is of utmost importance to prevent them. Being discontinuities inside the ingot, they can lead to cracking during forging and if not detected timely, may act as internal stress concentration sites ostensibly decreasing the fatigue strength and may cause catastrophic failure in service²¹. Figure 2.3 shows a set of freckles extending over the columnar dendrites region in a horizontal directionally solidified casting. Chen¹³ experimentally investigated the chemical composition of freckles found in a Ni-base superalloy ingot corresponding to commercial alloy 625. After hot working, freckles' macroscopic orientation and general characteristics still prevailed, as expected, and could be easily traced on a billet forged to 16 in. square

section from a 33 in. diameter ingot. Table 2.1 shows the obtained chemical composition of the as-cast ingot and the chemical composition of the phases found within the typical freckle channel. In general, high amounts of delta phase (δ -Ni₃Nb), laves phases and porosity were found.

Fig. 2.3-Freckles in horizontally solidified castings of simplified (a) and commercial Ni-base superalloys (b)¹⁴.

Similarly, segregated chemical composition on freckle channels was measured by Yu *et al.*²² for the case of superalloy 718. A considerable amount of laves phases was also observed, and the segregated material inside the channel had consistently higher amounts of Niobium and Titanium.

Table 2.1- Composition (Wt.%) of freckle channel segregates^{13,22}

(Wt.%)	Ni	Cr	Fe	Mo	Nb	Ti	Al	Si
Matrix 625	Bal.	22.09	4.4	9.10	3.53	0.29	0.26	0.03
δ -Ni ₃ Nb	67.28	5.19	1.11	4.74	19.98	0.84	0.85	-
Laves	30.11	18.2	2.06	27.77	21.25	0.30	0.3	-
Matrix 718	Bal.	18.58	17.62	3.38	5.46	0.97	0.67	0.12
Freckle - 718	52.55	17.36	15.23	3.51	9.43	1.33	0.43	0.16

The physical metallurgy of Ni-base superalloys is a major field of research and details are available in textbooks and numerous technical publications.^{23,24} It is believed that the systematic approach used for chemical composition design in the formulation of new single crystal alloys should also be useful in the development of novel wrought alloys with increased castability. Nevertheless, processing optimization should advance concomitantly with the new developed compositions as well as with the increasing demand of the traditional alloys like 718, since the macrosegregation defects incidence involves not only the material chemistry, but is strongly influenced by the physical phenomena involved during manufacture. After many years of dedicated research, the complexity of the interacting phenomena giving origin to macrosegregation defects still

impose a challenge to scientists on the fundamental academic aspects, as well as on the practical industrial applications.^{25,26}

2.3 Characteristics of Freckles in Alloy 718 VAR Ingots

Channel segregates found on VAR ingots received the name ‘freckles’ due to their dark spots appearance in the etched cross sections during macroscopic metallographic analysis. Their different chemical composition with respect to the bulk material and presence of porosity makes them easy to recognize by the conventional macroetching techniques. Differently from the freckles found on directional solidification of single crystal superalloy castings, which are preferentially located at the surface and aligned with the gravity direction, freckles found in VAR ingots are usually located in the midradius area of the ingots and with different orientations. It was found that their orientation is correlated to the density of the material solidified within the channel or freckle trail. When the density is higher than the bulk (like in the cases of alloy 718 or high speed tool steels) freckle channels are oriented closely aligned with the liquidus isothermals. When the material within the freckle has lower density than the bulk (as in the case of some austenitic stainless steels) they are parallel to the direction of gravity.²⁷ Fig. 2.4 shows the cross section of a VAR ingot made of alloy 718 (left), where the freckling region is recognized at the midradius area, and in the right side a longitudinal section of an alloy 718 ingot shows freckles alignment with the isotherms.

Fig. 2.4-Freckles in VAR ingots of alloy 718. Left: cross section macrograph from a 0.508 [m] diameter ingot⁹. Right: Longitudinal section macrograph of a 0.520 [m] diameter²⁸.

Closer observations made by Chen revealed that the freckles formed in VAR ingots show characteristics at a finer scale not observed in the superficial freckles found on directional solidified castings. It was pointed out that freckle channels had sharp boundary surfaces on the bottom (toward the direction of gravity), where the laves phases rich in Niobium are preferentially located, while the top boundary surface of the channel was more diffuse

with higher porosity. Fig. 2.5 gives an example for these observations for a strongly etched VAR freckle. It was suggested that the freckling mechanism explaining the formation of freckles in VAR ingots should take these morphological characteristics into account.

Fig. 2.5- Boundary fine scale morphology characteristics of freckles found in VAR ingot¹³

2.4 Mathematical Modeling of the Transport Phenomena During Solidification of Metallic Alloys

Pure metals and eutectic composition alloys solidify isothermally at the melting point temperature and at the eutectic temperature respectively. Differently, solidification of general alloys occurs not at a single value but over a range of temperatures. Typically, a transition zone called mush is formed at which solid and liquid phases coexist in an intricate solid dendritic array saturated with molten metal. Let a metallic binary alloy A-B with hypoeutectic composition C_0 (Wt. %) be at molten state, at a temperature sufficiently higher than its correspondent liquidus temperature T_L . If the crucible has low heat conductivity and is cooled from the bottom surface, equilibrium phases eventually will show the spatial distribution represented in Fig. 2.6. (A section of the hypothetical phase diagram is included for reference). Assuming that heat flow is one dimensional, the solid phase region and the mush layer will develop a flat lower boundary at temperature T_s which corresponds to the *solidus* point of the alloy and the fraction liquid f_L (referred also as g_L) is equal to zero, while the fraction solid f_s is equal to one (also represented by ϕ or g_s). With increasing distance along the z -axis it is noted that the volume fraction of liquid f_L increases in the mush layer until it becomes unity (solid fraction decreases to zero) at a distance H from the lower boundary of the mush. In that location, temperature

is equal to T_L and defines the position of the plane associated with the interface mush-bulk liquid.

Due to the continuous heat transfer and progress of solidification, the isotherms and hence the boundaries move along the z -axis at the rate of growth of crystals R . In practice, during directional solidification processing the furnace maintains the selected temperature gradient fixed in position, while the crucible containing the solidifying metal is pulled down at an appropriate growth rate.

Fig. 2.6 Representation of the mush layer on directional upward solidification

During solidification, atoms of the solvent are selectively taken from the parent liquid to form the crystals that make up the dendrites. Hence, the liquid in the proximity of the solidification front is segregated by the ejected solute atoms. There are two hypothetical limiting cases for the extent of microsegregation of the interdendritic liquid during solidification. The first case occurs if thermodynamic equilibrium exists during solidification, that is, solid and liquid compositions at the interface are given by the phase diagram. Consequently, the composition of the solid can be determined in terms of the fraction solid formed from equation [2.1], where k corresponds to the partition coefficient of the solute given by $k = C_s/C_L$ and C_0 is the nominal solute content of the parent liquid.

$$C_s = \frac{kC_0}{f_s(k-1) + 1} \quad [2.1]$$

The solidification under equilibrium conditions assumes that there is infinite diffusion of the solute in the solid and liquid phases. The second limiting case considers no diffusion of solute in the solid phase, and infinite diffusion of solute in the liquid phase. With those conditions, the composition of the solid phase with respect to the solid fraction formed is given by the Scheil equation, which can be written as:

$$C_s = kC_0(1 - f_s)^{(k-1)} \quad [2.2]$$

A great number of research efforts are dedicated to obtain accurate predictions of the microsegregation measured experimentally. Models using analytical and numerical approaches have been proposed to include the effect of back diffusion of solute to the solid phase, the transport of solute by convection/diffusion in the near interdendritic

liquid, interdendritic liquid undercooling, and coarsening of the dendrite arms among others.^{29,30} In many cases, when the solidification occurs near equilibrium, the phase diagram can be used to describe the thermodynamical state with appropriate accuracy; and if further simplifications are required, it is common to find that the liquidus and solidus curves are deemed to be linear. That is, the partition coefficient k is considered constant. The assumed linear relation between the composition of the interdendritic liquid and the local temperature is given by equation [2.3] where T_E is the eutectic temperature of the hypothetical binary alloy; C_E is the corresponding eutectic composition for the system and Γ is the constant slope of the liquidus.

$$T = T_E + \Gamma(C - C_E) \quad [2.3]$$

With the positive temperature gradient established in the system represented in Fig. 2.6, an associated density distribution develops in the liquid phase. At the same time, due to the above mentioned partition of the solute elements and microsegregation, the interdendritic liquid shows a compositionally induced density gradient. Usually, the influence of the compositional variation of density is dominant in the mush and that is why the solute partition coefficient is very important. The effects of temperature (T) and composition (C) over the density are determined by equation [2.4].

$$\rho = \rho_0 \times [1 - \alpha^* (T - T_L) + \beta^* (C - C_0)] \quad [2.4]$$

Where ρ_0 is the density of the alloy at liquidus temperature T_L , α^* is the thermal volume expansion coefficient, and β^* is the solutal volume expansion coefficient. Usually α^* is positive, meaning that the density increases with decrease in temperature, while β^* could be either positive or negative depending on the solute segregating in the mushy layer. When the value of β^* is negative and its associated effect is greater than the temperature associated term, the density of the interdendritic liquid at mush regions will be smaller than the density of the bulk liquid, and then, a buoyancy driving force is set up for convection. Fig. 2.7 shows a representation of the density distribution in the system considered above, when β^* is negative.

Fig. 2.7- Liquid density distribution in the mush and bulk liquid region

As briefly mentioned in section 2.2, the interaction between the interdendritic liquid flow and the solid array involves transport of heat and solute that can change the dynamics of dendritic growth producing enhanced or delayed growth, remelting, detachment, and in general, may strongly perturb the local solid fraction and consequently affect the final microstructure of the casting.³¹ The transport of mass, momentum, energy and species during solidification can be mathematically described by considering a single or multi-region domain. A single region domain, takes the whole space occupied by the solidifying material as the system under analysis, and uses a single set of conservation equations that equally applies for every point. A multi-region domain separates the system as composed by different zones: solid, mush and bulk liquid, and uses different local sets of conservation equations for each case, while the overall solution is obtained by complementing these sets of equations with the corresponding boundary interaction relationships. Single domain approach has found more acceptance and continued development since it gives the possibility of using computational tools to obtain numerical approximate solutions without the additional task of keeping track of the evolving boundaries. In fact, one of the complications in the analytical solutions based on multi-region domain is that the height of the mush needs to be determined with the set of unknowns.

Besides the general characteristics already mentioned, there is a fundamental concept that is included in virtually all mathematical modeling of the transport phenomena during solidification of alloys. It is assumed that the mush layer is composed of two interpenetrating phases, *i.e.*, the ‘forest’ of solid dendrite crystals and the interdendritic liquid filling all the interstices, and that each phase can be described by the usual field quantities, which are continuous in that phase at the micro-scale, but discontinuous on the entire space. It is assumed that the state of the system in the microscopic scale is then governed by the usual continuity equations combined with the appropriate interfacial boundary conditions. However, the solution of the conservation equations is not practical because of the highly convoluted topography of the interfacial surface. To solve this, the scale at which the system is described must be modified and resort to the fine internal structure of the mush region is made to treat it as a single continuum phase.³¹ The description scale is altered by averaging the microscopic conservation equations over some representative elementary volume. This, results in the establishment of macroscopic conservation equations that in conjunction with constitutive relations, can be used to solve practical engineering problems.³²

The constitutive relations describe the interactions between phases linking the so-called interfacial transfer terms, which appear during the averaging process, to the macroscopic transport. Consequently, the constitutive relations have the important function of establishing a way to incorporate microscopic processes such microstructure development, interfacial stresses, and interfacial heat and mass transfer.

The volume averaging methodology requires a careful selection of the representative volume element size. It needs to be sufficiently big to include complete microscopic information but small enough as to remain differential within the hypothesis of a continuum, so the averaged quantities could be represented by continuous functions of

space and time. For example, it was postulated by Flemings and Nereo³³ that the solid fraction within the elementary volume should be equal to the local volume averaged value. The macroscopic length scale is of the order of 10^{-1} to 10^0 m, and the microscopic features of the mushy zone are of the order of 10^{-6} to 10^{-5} m.

In consistency to the size conditions, the elementary volume length scale is usually of the order of 10^{-3} to 10^{-2} m, which is fortuitous because matches the average size of the typical computational element resulting from the discretization of the domain in numerical simulations. The averaging procedure sometimes is explicitly explained in the establishment of the models, while in others it is intrinsic or just tacitly implied.

2.4.1 Local Solute Redistribution Equation

In a series of articles published at the end of the 1960s decade, Flemings and co-workers^{33,34,35} developed an expression to calculate the macrosegregation caused by interdendritic flow driven by thermal and solidification contractions. It was considered a differential elementary volume as mentioned above with a set of complementary suppositions to obtain analytical solutions for quantitative comparisons with experiments. The additional assumptions included: no solid enters or leaves the differential element, solute only crosses the boundaries due to liquid flow induced only by solidification shrinkage or thermal contractions, liquid composition and temperature within the element are uniform at any time t , the solid phase density is constant, and there is no porosity. Given the importance of the local solute redistribution equation on the formulation of mathematically based freckle criterions, its complete derivation is included in appendix A. The local solute redistribution equation is presented as follows:

$$\frac{\partial g_L}{\partial C_L} = -\left(\frac{1-\beta}{1-k}\right)\left(1 + \frac{\bar{v} \cdot \nabla T}{\epsilon}\right) \frac{g_L}{C_L} \quad [2.5]$$

Equation [2.5], even when used in combination with an arbitrary linear distribution of fraction liquid with temperature over the mush layer, was successful to describe quantitative macrosegregation induced by casting design parameters affecting the heat flux in time or by sudden changes in the heat transport, like the formation of a gap between the solid casting surface and the mold due to shrinkage.³⁴

Mehrabian *et al.*^{36,37} complemented the local solute redistribution equation by adding the gravitational effect. The macrosegregation related to fluid flow was quantitatively studied for the first time considering transport due to the solidification and thermal contractions, and the effect of gravity acting on a fluid of variable density. By further analysis of the equation of local solute redistribution, a flow instability discussion was included to predict if an incipient channel from a regular group, which has a perturbed greater diameter will unstably continue growing or not. The conclusions drawn established the base to what became to be known years after as the Flemings' criterion for freckling.

The analysis starts by multiplying equation [2.5] by the partial derivative $(\partial C_L / \partial T)_{x,y,z}$ to obtain equation [2.6]:

$$\frac{\partial g_L}{\partial T} = -\left[\frac{1-\beta}{1-k} \cdot \frac{g_L}{C_L} \cdot \frac{\partial C_L}{\partial T}\right]\left(1 + \frac{\bar{v} \cdot \nabla T}{\epsilon}\right) \quad [2.6]$$

Anytime the left hand side (LHS) of equation [2.6] is positive, ($\partial g_L / \partial T > 0$), implies that the solid volume fraction increases with decreasing temperature, which means that solidification reaction progresses. Since the quantity inside the brackets on equation [2.6] is negative (Due to the liquidus relation on the hypoeutectic compositions), the flow of interdendritic liquid from hotter to colder regions always stabilized any perturbation in the size of the channels, due to the fact that the inequality [2.7] turns to be valid. Any channel with greater size than its neighbors, will host a flow with increased velocity value which will lead to faster solidification, and hence its size will trend to decrease again to the stable value.

$$\left(\frac{\bar{v} \cdot \nabla T}{\varepsilon} \right) > 0 \quad [2.7]$$

If the increased size channel perturbation occurs when the flow is in the direction from the cold region to the hot region, inequality [2.7] does not hold valid. Two different results are taken into account by visualizing the effect over the parenthesis term in the RHS of equation [2.6]. If $0 > (\bar{v} \cdot \nabla T / \varepsilon) > -1$, then solidification reaction still progresses ($\partial g_L / \partial T < 0$), and the increased flow through the unstable bigger diameter channel will induce its reduction in size. Lastly, if $(\bar{v} \cdot \nabla T / \varepsilon) < -1$, the factor in parenthesis on the RHS of equation [2.6] will be negative, and hence $\partial g_L / \partial T < 0$, which means remelting occurs and the channel will unstably increase in size with decreasing temperature creating a macroscopic channel type defect.

Besides the contribution of the gravitational effect for the model construction and the instability of channels analysis; Mehrabian *et al*'s publication, contributed to unfold for the specific application, the use of computer assisted numerical solutions to release the limitations imposed by the analytical solutions.³⁶ It is opportune to mention here that the development of solidification simulation models and computer codes to assist the manufacture process design had a relative slow evolution when compared to the use of computational tools in the solid mechanics area, essentially due to the complication of the presence of the reacting liquid phase.³⁸ Only after more than one decade passed it was held the first Symposium on Modeling of Casting and Welding Processes.

2.4.2 Volume Averaging Method

To review the fundamental aspects of the volume averaging technique, the classical definitions, theorems and identities are presented along with the final forms for the conservation of mass and momentum equations³². The derivation of these equations is summarized in appendix B. The equations of conservation of mass and momentum are essential because they have a direct involvement with the mechanics of freckle formation. The procedures typically followed for the conservation of energy and species are supported in the same conceptual frame and their detailed development could be found in many articles.^{39,40,41}

Consider an averaging volume on the mush dV (representative elementary volume - REV) bounded by an averaging area dA (representative elementary area - REA), with a centroid located in the internal point C as represented in Fig. 2.8. The position of the centroid with respect to coordinate system $OX_1X_2X_3$ is given by vector x . An arbitrary

point P in dV has a position with respect to the fixed coordinate system given by vector $\mathbf{r}$, while its position with respect to the centroid is given by vector ξ .

Fig. 2.8 Elementary averaging volume in the mush

Any microscopic tensor ψ (density, enthalpy, temperature, velocity, stress, etc) describing a property of the liquid (ψ_L) or solid phase (ψ_S) with a field distribution within the microscopic averaging volume dV (for arbitrary point P) has a corresponding macroscopic representative average Ψ_L or Ψ_S associated to the centroidal point C.

The equations of conservation in the macroscale are constructed by using the classical theory of continuum mechanics⁴² and the averaging process is included in the appendix B. The final expression for the conservation of mass is given by equation [2.8], where $\mathbf{V}_L$ vector represents the averaged liquid velocity.

$$\nabla \cdot \vec{V}_L = 0 \quad [2.8]$$

Similarly, following the derivation presented in appendix B, the averaged conservation of momentum equation becomes:

$$\rho_L \left[\left(\frac{1}{g_L} \right) \frac{\partial \vec{V}_L}{\partial t} + \left(\frac{1}{g_L^2} \right) \vec{V}_L \cdot \nabla \vec{V}_L \right] = -\nabla P_L^L + \rho_L \vec{g} + \left(\frac{\mu}{g_L} \right) \nabla^2 \vec{V}_L - \mu \left[\left(\frac{1}{\underline{K}^{(2)}} \right) \cdot \vec{V}_L + \frac{\underline{C}^{(3)}}{g_L^3} : (\vec{V}_L)(\vec{V}_L) \right] \quad [2.9]$$

Where P_L^L is the intrinsic volume average pressure, μ is the averaged viscosity of liquid, vector $\vec{g}$ is the gravity acceleration, $\underline{K}^{(2)}$ is a symmetric anisotropic tensor of second order representing the permeability of the mush, and $\underline{C}^{(3)}$ is a third order resistance tensor. Both $\underline{K}^{(2)}$ and $\underline{C}^{(3)}$ are depend on the morphology characteristics of the solid dendritic array like the interdendritic spacing, volume fraction of solid phase, coarsening, etc.

The fourth term on the RHS of equation [2.9] includes a third order resistance tensor $\underline{C}^{(3)}$ that should be determined experimentally. This term is proportional to the square of the interdendritic liquid velocity, and because the interdendritic liquid flow is slow, it is frequently neglected. When solid motion is considered it could be demonstrated that $\underline{C}^{(3)}$ is proportional to the relative velocity between solid and liquid phases.

The volume averaging method can also be used for systems with more than two phases in dV . For example, Wang *et al*⁴⁰ have used this approach to treat separately the near-interdendritic liquid from the rest of the liquid phase inside dV in order to give closer detailed analysis to the microscopic events. This approach has been found especially useful to avoid ‘smearing’ of important microscopic phenomena such nucleation, undercooling, and to incorporate the models for growth of the tip of dendrites. Further examples of using multiple phases in dV include porosity formation, presence of inert particles⁴³ and castings of composite materials. The method considers that each phase k in dV occupies a volume dV_k . The part of dV occupied by phase k is bounded by the interfacial area A_k which has outwardly directed normal unit vector n_k and w_k is the velocity vector of the interface. The phase distribution function (analogous to γ function in appendix B) is defined as X_k and is equal to unity in phase k and zero otherwise. Then, the volume average value $\langle \psi_k \rangle$ of a microscopic quantity ψ_k of phase k is given by equation [2.10]:

$$\langle \psi_k \rangle = \left(\frac{1}{dV} \right) \int_{dV} \psi_k X_k dv \quad [2.10]$$

By letting $\psi_k=1$, the expression for the volume fraction of phase k is obtained in equation [2.11] and consequently equation [2.12] is valid when no porosity is formed.

$$g_k = \frac{V_k}{dV} \quad [2.11]$$

$$\sum_k g_k = 1 \quad [2.12]$$

The volume averaging technique is considered to have advantage with respect to other methods because the relationships between the microscopic equations and their corresponding averaged expressions in the macroscale are explicit and can be further elaborated without recurring to completely empirical expressions.⁴⁴ As mentioned in section 2.4, the complementary constitutive relations associated with the interfacial balances that appear during the averaging process (like the areal integral terms in equations [B.9] and [B.10] in the appendix section) give crucial links to incorporate the evolution of the solid structure and the transport phenomena on a microscopic level to the macroscopic description.⁴⁵

2.4.3 Application of Diffusive Mixture Theory

Bennon and Incropera⁴⁶ obtained a set of macroscopic conservation equations by using the classic theory of diffusive mixtures. The fundamental concepts on which the method is based are: the components of the mixture are treated as independent subsystems and their interactions need to be taken into account appropriately, the mixture macroscopic quantities are described by the mathematical result of the combined properties of the components in the mixture, and the equations governing each component physics have correspondent versions describing the collective behavior of the mixture. Originally, the theory assumes that the components are inert, so for extending its application on solidification where the components are non-inert, it is required to involve relationships that account for the behavior of the constituents in the atomic scale as the phase diagram, fictitious volume fractions for the reacting constituents and empirical relationships regarding internal interactions of a constituent with itself. As classically defined, a

constituent (α) represents a basic chemical element or a compound, whereas a phase (k) represents a certain amount of matter that is homogeneous in microstructure, distinctively separable in the continuum and could be composed by a single or multiple constituents. A phase not necessarily should be homogeneous in chemical composition. In this conceptual frame, the representative elementary volume similar to the one depicted in Figure 2.8 could be regarded as a continuum composed of (α) constituents distributed on (k) separable phases. The mean velocity of all constituents in phase k is represented by the phase velocity vector V_k . Meanwhile the so-called absolute (total) velocity of constituent α in phase k is represented by V_k^α , and the velocity of constituent α relative to the velocity of its phase k is the diffusion velocity of α and is given by $(V_k^\alpha - V_k)$. Similarly, the actual density of constituent α in phase k and the volume fraction of constituent α in phase k are given by ρ_k^α and g_k^α respectively. Equation [2.28] expresses the partial density of constituent α in phase k as follows:

$$\bar{\rho}_k^\alpha = g_k^\alpha \rho_k^\alpha \quad [2.13]$$

Regarding phase k , its actual density and volume fraction within the continuum are expressed by ρ_k and g_k by respectively. The partial density of phase k , which could be regarded as its contribution on the density of the total representative volume is given by equation [2.14]

$$\bar{\rho}_k = g_k \rho_k \quad [2.14]$$

The mass fraction of constituent α in phase k and the mass fraction of phase k are defined by equations [2.15] and [2.16] respectively:

$$f_k^\alpha = \frac{\bar{\rho}_k^\alpha}{\rho_k} \quad [2.15]$$

$$f_k = \frac{\bar{\rho}_k}{\sum_k \bar{\rho}_k} \quad [2.16]$$

Since the change in volume fraction of one phase is at expense of another phase within the elementary volume and should not vanish simultaneously, the equality of equation [2.17] is established:

$$\sum_k g_k = 1 \quad [2.17]$$

With all the preliminary relations defined, the conservation of a general specific quantity ϕ_k associated with the phase k in the representative control volume V of surface A (analogous to the REV and REA in section 2.1.2), is given by the balance between the accumulation, net flow by advection and diffusion, and its volumetric generation according to equation [2.18]:

$$\frac{\partial}{\partial t} \int_V [\rho_k \phi_k] dV_k + \int_A [\rho_k \vec{V}_k \phi_k] \cdot \vec{n} dA_k = \int_A -\vec{J}_k \cdot \vec{n} dA_k + \int_V S_k dV_k \quad [2.18]$$

Where the unit vector $\vec{n}$ is the outward normal vector to the surface A , vector $\vec{J}_k$ is the flux of quantity ϕ_k through A , and scalar S_k is the volumetric source which takes into account the generation or annihilation of ϕ_k , and the area A_k is assumed given by the product $g_k dA$. Since the volume V is arbitrary, the differential form of equation [2.18] is valid and is given by equation [2.19] after applying the classical calculus theorems of Gauss and Leibnitz:

$$\frac{\partial}{\partial t}(\bar{\rho}_k \phi_k) + \nabla \cdot (\bar{\rho}_k \vec{V}_k \phi_k) = -\nabla \cdot (g_k \vec{J}_k) + g_k S_k \quad [2.19]$$

With equation [2.19] the equations of conservation of mass, momentum, energy and species for phase k are obtained by replacing appropriately the tensor representations of ϕ_k , J_k and S_k . The total conservation equations are obtained by summing the individual phase equations for all phases within V . As mentioned above, closure of the system of conservation equations is obtained by using supplementary relationships; in particular, the phase diagram is fundamental to relate the phase compositions with temperature.

Although valuable advances have been obtained on the evolution of thermodynamical microscopic models and numerical simulations on the macroscale, coupled phenomena descriptions at scales ranging several orders of magnitude are still a great challenge. It is believed that new methods are required to maintain the complete required detail at the fine length scale while allowing solutions at reasonable cost from the computational point of view.³⁸

2.5 The Mush Layer Conceived as a Porous Media and Permeability Tensor

Mehrabian *et al.*³⁶ proposed the use of porous media theory to describe the velocity of the interdendritic liquid in the mush through the Darcy law⁴⁷. The validity of this treatment is assured because the flow of the interdendritic liquid is slow with negligible inertia effects at the microscale so linearity is maintained. Given the empirical origin of the Darcy law, a macroscopic averaged description is tacitly conceived for the microscale liquid - solid interactions.

The permeability in the mush layer plays a fundamental role in the mechanics of the interdendritic liquid flow that causes macrosegregation. Basically, it represents the impedance to the flow and together with the acting driving forces, determines if unstable convection will evolve. The mush layer permeability tensor is a function of position and time, and due to the directional morphology of the columnar dendritic array, it has anisotropic nature. This characteristic is expected since the dendritic array has different spacings between the primary arms (λ_1) with respect to the spacings between the secondary arms (λ_2). (Primary Dendrite Arm Spacing-PDAS also is referred as d_1 , while the Secondary Dendrite Arm Spacing-SDAS is alternatively referred as d_2). Particularly, because the dendrites have a four-fold symmetry, the permeability is a symmetric, transversely isotropic tensor, which turns to be advantageous for using two dimensional domain simplifications. It has been proven by experimentation that increasing cooling rates in the mush decrease the interdendritic spacings while the increase of solute content on the microsegregated liquid tends to increase the interdendritic distances^{48, 49}. Poirier⁵⁰ performed experiments using Pb-Sn and borneol-paraffin alloys to obtained empirical multilinear regression equations for the permeability tensor components in the parallel (K_p) and normal direction (K_n) to the primary dendrites (which are aligned with the temperature gradient vector). The parallel and normal directions to the primary dendrites arms were assumed as constituting the principal directions of the permeability tensor and equation [2.20] is used when the permeability is referred to the principal axes (coordinate axes oriented along the orthogonal principal directions). This assumption is justified,

given the fact that the experimental apparatus used confines the measured flow to the same direction on the applied pressure gradient and the samples used were directionally solidified so the orientation of the columnar dendrites is known *a priori* and properly selected before the corresponding tests. Poirier's equations best fit the experimental data for liquid fractions between 0.19 and 0.66 and are presented as follows:

$$\underline{K} = \begin{bmatrix} K_I & 0 & 0 \\ 0 & K_{II} & 0 \\ 0 & 0 & K_{III} \end{bmatrix} \quad [2.20]$$

$$K_{II} = K_{III} \quad [2.21]$$

$$K_I = 3.75 \cdot 10^{-4} \cdot f_L^2 \cdot \lambda_1^2 \quad [2.22]$$

$$K_{II} = 3.62 \cdot 10^3 \cdot f_L^{3.34} \cdot \lambda_1^{0.699} \cdot \lambda_2^{2.73} \quad [2.23]$$

where λ_1 [m] is the PDAS, λ_2 [m] is the SDAS and f_L is the liquid fraction. The relation between the parallel component of permeability K_I and the square of the PDAS (λ_1) in equation [2.22] was found to be in agreement with previous experiments performed by Streat and Weinberg⁵¹. When the model of a bundle of straight capillars was used to describe the parallel component, Streat and Weinberg found a tortuosity factor of 4.6 for the hypoeutectic alloy Pb-20 Sn evaluated. On the other hand, experiments developed by Murakami *et al.*⁵² using borneol-paraffin system showed that the normal permeability is proportional to the square of the PDAS and to the cube of the liquid fraction.

Oryshchyn and Doğan⁵³ found that the degree of anisotropy of the permeability tensor depends on the alloy system. It was found that at the same liquid fraction, the anisotropy degree of Fe-2Cr-0.5C was greater than the anisotropy degree in Al-5Cu. This dependence of the permeability to the alloy system has also being intuited by knowledge over years of experience by metallurgy scientists⁵⁴, but have not been sufficiently addressed with experimental verification to the author's knowledge. In fact, most of the quantitative calculations for convective flow on superalloy mushy zones use the experimental equations for permeability obtained from experiments using low melting point alloy systems.

Because the dendrite arms are too fragile at higher liquid fractions, experimental approach to determine the permeability components does not give significant data. To find expressions for the permeability components at liquid fractions greater than 0.65, Bath *et al.*⁵⁵ used numerical simulations to obtain the velocity fields and infer the permeability in the normal direction K_{II} by approximating the dendrites cross sections to simple shapes like cruciforms. In this fashion, piecewise functions have been defined for the permeability components along the mush. However, the expressions provide discontinuous descriptions that in some simulations induced discrete jumps of about two orders of magnitude in the calculated interdendritic liquid velocity fields near the liquid

fraction of the transition ($f_L=0.7$). Fig. 2.9 shows an example of the unrealistic jump in the definition for the anisotropic components of permeability.

Fig. 2.9 Variation of the permeability components and the permeability ratio with the liquid fraction ($\epsilon_L=f_L$, $K_I=K_{\xi\xi}$ and $K_{II}=K_{\eta\eta}$)⁵⁶

2.6 Mechanisms of Freckle Formation

In this section, the description of the proposed freckling mechanisms is reviewed by considering the vertical unidirectional solidification of the hypoeutectic binary alloy of Fig. 2.6.

2.6.1 Density Inversion

As previously mentioned, after the positive thermal gradient ($\partial T/\partial z$) is imposed and solidification process evolves, composition and density gradients develop along the mush layer as a result of the partitioning of solute elements. If light elements are rejected toward the liquid phase or the heavy elements are depleted from the interdendritic fluid, then density gradient ($\partial \rho/\partial z$) will be positive along the mush (density inversion condition). This positive gradient extends up to a plane right above the tip of the primary dendrites, including a thin boundary layer of segregated liquid that builds ahead of the solidification front as schematically depicted in Fig. 2.7. The density gradient changes sign at the top of the boundary layer and density decreases at higher positions in the bulk liquid region, farther from the chill.²⁷

Inside the mush layer, the buoyancy forces may become sufficiently strong to overcome the frictional resistance offered by the dendritic array and upward flow of interdendritic liquid will occur. Because of the considerable difference between the thermal diffusivity

and the mass diffusivity, the interstitial liquid transported to higher temperature positions has a faster capacity to equilibrate its temperature than its composition with the new surroundings and remelts/erodes the already formed dendrite arms. The regions with perturbed solid fraction and upwelling segregated liquid evolve to chimneys, through which plumes of interdendritic liquid are projected into the bulk liquid, and lastly may solidify as the defects known as freckles.

This overall mechanism is widely accepted and has been supported by experimental observations and numerical simulations on analogous transparent systems and metallic alloys.^{44, 57} Single crystal alloys for turbine blades with a high content of refractory elements are especially susceptible to freckles formed by this mechanism, as well as some cast and wrought superalloys like Waspaloy⁵⁸. Details about the nucleation and propagation of freckles caused by upward flow of segregated interdendritic liquid have been studied extensively by experiments on analogous translucent systems as ammonium chloride aqueous solutions ($\text{NH}_4\text{Cl}+\text{H}_2\text{O}$). The detailed sequence of events interpreted (although stages certainly overlap) starts with the growth of a continuous solid on the chilled surface and the initial growth of the mush layer. The boundary layer of segregated liquid on top of the primary dendrites becomes gravitationally unstable and double diffusive fingers evolve on the interface mush-bulk liquid. This fine scale convective pattern is followed by the appearance of larger convective plumes that increment in strength and number. With time, strong convective plumes are accompanied by chimneys formation in the mush. The number of chimneys decreases because of competence for downwelling liquid from the bulk and some channels are choked by the advance of the crystallization front. At the end of solidification, the remaining channels will be preserved as vertical zones containing highly segregated material with the lowest melting point.⁵⁹

Although acceptance of thermosolutal convection origin of freckles in upward solidification is fairly generalized, universal agreement about their specific nucleation points and evolution has not been reached. Sample and Hellawell⁶⁰ proposed that channels originate at the growth front and propagate back into the mush. For the channels to form, it is required that the boundary layer convective pattern to induce perturbations on the solid fraction and the local liquidus temperature at the proximity of the primary dendrites tips. Numerical simulations and experiments have been used to support this proposed nucleation site and evolution.^{60,61, 62, 63, 56}

On the other hand, Worster⁶⁴ used linear stability analysis of thermosolutal convection on “ideal” mush layers and proposed that two possible modes of convection can occur independently. The first mode called boundary layer mode corresponds to the mentioned double diffusive fingers on the interface mush-bulk liquid, which leaves the fluid in the mush stagnant, whereas the second convection mode denominated mush layer mode happens within the mush and causes perturbations in the solid fraction that lead to the formation of chimneys.^{59,64,65} The hypothesis of nucleation of the channels inside the mush layer also is supported by theoretical and experimental results.^{66,67, 68}

Experiments supporting the mechanism of freckles nucleation at the tips of the dendrites region are based on induced shear movement of the bulk liquid at the boundary layer vicinity. The experimental arrangements used consist on a cylindrical mold chilled in the bottom, with upward directional solidification of analogous systems like $\text{NH}_4\text{Cl}-\text{H}_2\text{O}$ and

Pb-Sn. The shear displacement of the bulk liquid layers near the solidification front is created by precession using rotation of the mold ($< 5\text{rpm}$) around an inclined axis (25 deg from the vertical) or by spin-up / spin-down sequences around a vertical mold developing an Ekman layer (like the convection patterns induced in a vertical washing machine). It is concluded that the effect of blocking the evolution of channels is due to the disruption of the double diffusive convective cells in the boundary layer that are required for the channels to grow from the top of the dendrites downward into the mush. However, it could be argued that the experiments support the model of nucleation of channels inside the mush as well, by interpreting the effect of shearing as breaking the entrance of bulk liquid into the mush, so the channels do not evolve within the mush because there is not enough reposition liquid for a continuous flow to evolve.

2.6.2 Downward Flow

If the density gradient is negative, it will be gravitationally stabilizing and the liquid in the mush and in the bulk liquid region will be stratified and no density inversion will be present. When the heat flux is not aligned with gravity, the solidification front is not perpendicular to the gravity vector and it has been proposed that the heavier liquid in the mush will tend to seep between the dendrites, following a path almost parallel to the liquidus isotherm melting/eroding the dendrites on its path and give origin to the freckles seen on VAR ingots.^{28, 69}

The proposed mechanism for freckling in VAR ingots has been conceived mostly based on the observed morphology and characterization of freckles in solidified ingots. Auburtin *et al.*⁷⁰ used freckles composition determined by Scanning Electron Microscopy/Energy-Dispersive Spectroscopy (SEM/EDX) and compared it with the segregation profiles to conclude that the freckles formed from a mush region between 0.4 to 0.6 solid fractions, which corresponded to the location of the isotherm 20 K below liquidus.

Considerably less detailed information is found in the literature regarding the sequence of events leading to the nucleation and growth of freckles in VAR when compared with the density inversion case. Freckles usually form in the midradius of the ingot and more frequently are found when the molten metal pool has a steeper “bowl shape” like in the ingots remelted during the Electro Slag Remelting process (ESR). Numerical simulations corroborate the foundry practice knowledge that abrupt variations on the controlling parameters of VAR induce perturbations in the temperature and composition of the interdendritic liquid that should have a strong influence on freckle nucleation and growth.^{71, 72, 73} Nevertheless, no direct simulation of freckles in VAR for industrial application has been accomplished, mostly because of insufficient high temperature physical properties data needed, lack of understanding of the effects from the microscopic scale processes and excessive computational requirements of the transient multiscale, multiphysics, models.

It has been proposed that horizontal directional solidification experiments better resemble the freckling conditions for VAR ingots.^{14, 74, 75} Results showed that freckles can propagate without the influence of the electromagnetic Lorentz force, indicating that it

would be possible that freckles in VAR ingots have a nucleation mechanism that is not necessarily linked to the bulk liquid convection patterns.

A better understanding of the freckling mechanism on VAR ingots is required to devise accurate predictions and more efficient prevention strategies. As noted by Asta *et al.*⁷⁶, much of the knowledge about the effects of the convection and its effect on the microstructure is fragmented or incomplete. The degree of complexity of the interaction between the convective flow and the microstructure is even increased by the experimentally demonstrated fact that convection depends on the microstructure (e.g. the permeability in the mush), but the convection affects the dendritic arm spacing and changes the permeability itself.^{49, 77}

2.7 Criteria for Freckle Prediction

Prediction of freckling has been attempted using different approaches. Mathematically derived criteria and predictions based on numerical solution of the continuity equations are the main tendencies as remarked by Auburtin.⁷⁸ The early criteria proposed were constructed by functional forms involving controlling operational parameters like the temperature gradient in the solidification front, rate of growth, and cooling rate.²⁷

As mentioned previously in section 2.1.1, Flemings and Nereo³³ developed a mathematical description of macrosegregation and postulated the so called local solute redistribution equation, which constituted the basis for the Flemings' criterion for freckling presented as the inequality [2.24]. Basically, it states that a freckle will form if the following inequality holds valid (*i. e.*, the liquid flow from colder to hotter regions is faster than the rate of crystals growth)³⁶.

$$\frac{\vec{v} \cdot \nabla T}{\varepsilon} \leq -1 \quad [2.24]$$

The criterion proposed by Flemings *et al.* presents a physical explanation of the remelting effect of the already established convective flow, but it requires linking the interdendritic flow with its causes, associated to the thermal-chemical conditions and geometrical aspects of the phenomenon. For that reason, some authors consider the Flemings' criterion as defining whether a channel will evolve unstably rather than as a criterion for the nucleation of a channel.^{63, 67}

Pollock and Murphy⁷⁹ found that for single crystal superalloy SX-1 it was possible to define a critical value, based on thermal conditions of directional solidification, below which the onset of defects was not expected. The condition is expressed in the subsequent equation [2.25] where G represents the gradient and R the growth rate.

$$G^{-1/2} R^{-1/4} \leq 0.95 \quad [2.25]$$

The criterion expressed by equation [2.25], has the inconvenience that it does not give any additional information regarding the location for the nucleation of the defects within the casting and it is difficult to extend to different compositions.

Because the interdendritic flow results from natural convective instabilities, the criterion with currently wider acceptance is the one based on the Rayleigh number concept. The

Rayleigh number could be defined as the ratio between the buoyancy and the viscous dissipation forces. For convection in the mushy zone, the driving force is essentially a result of compositional buoyancy and the viscous dissipation is related to flow impedance through the dendritic array. It has the advantage that incorporates the thermal and compositional effects over the freckling tendency. The value of the Rayleigh number criterion defining the threshold between the freckling and non freckling conditions is denominated critical Rayleigh number. If the Rayleigh number for a determined set of conditions is below the critical value, then freckles are not expected to form, but it is possible that the system could have a Rayleigh number higher than the critical value and yet no freckles being formed.⁸⁰

Although the Rayleigh number is adopted from the mathematical description of convection through the dimensionless system of continuity equations,³¹ no consensus has been reached regarding its formulation. Yang *et al.*⁸¹ reviewed a series of Rayleigh number criteria proposed by various authors and noted that the main difference between formulations lies in the meaning each author gave to the characteristic length of the system.

Beckermann *et al.*⁸² presented a criterion based on the maximum Rayleigh number using a formulation similar to the one deduced by Worster⁶⁴ and expressed by equation [2.26], where $(\Delta\rho/\rho_0)$ is the relative density inversion, g is the gravity, K is the averaged permeability, h is the distance measured from the top of the mush to the point of interest, α is the thermal diffusivity and ν is the kinematic viscosity.

$$Ra = \frac{(\Delta\rho/\rho_0) \cdot g \cdot K \cdot h}{\alpha \cdot \nu} \quad [2.26]$$

To validate their formulation, full numerical simulations were performed with the parameters used on each of the upward solidification experiments by Pollock and Murphy⁷⁹ on Superalloy SX-1, and the local Rayleigh numbers calculated at the initiation sites of simulated freckles were considered as the critical values. The corresponding average was compared with the threshold value (transition value between freckle and no-freckle) obtained from the set of maximum Rayleigh number values calculated from the original experimental data. A critical averaged value of 0.25 was determined from the simulations with vertical domains and it was consistent with the values determined on complementary simulations for other single crystal superalloy compositions. The difference between the threshold obtained from the experiments and the simulations was considered within the uncertainties related with the experimental thermal parameters. Additionally, it was shown that the inclination angle with respect to gravity decreased the threshold values.⁸³ Beckermann *et al.*'s contribution has the disadvantage that its application for VAR ingots freckling prediction is limited because its derivation is focused on the upward flow mechanism caused by density inversion, and its validation assumed that the freckles should form in the solidification front proximity (fraction solid < 0.2). Yang *et al.*⁸¹ presented a freckle criterion for upward directional solidification of alloys. Their approach consisted of developing a Rayleigh number criterion from the Flemings form by considering the mushy layer as a porous media with variable permeability and assuming that the interdendritic flow could be described by the Darcy law. Their proposed form is presented in equation [2.27] as follows, where $\Delta\rho$ is the

relative density change as previously defined, g is the gravity, Π is the permeability, ν is the liquid kinematic viscosity, f_L is the liquid volume fraction and R is the crystal growth rate.

$$Ra = \frac{(\Delta\rho) \cdot g \cdot \Pi}{\nu \cdot f_L} \cdot \frac{1}{R} \quad [2.27]$$

The approach assumed the permeability as a scalar defined by Poirier's formula for flow parallel to the primary dendrites direction.⁵⁰ Their criterion was evaluated using directional solidification experimental data for Pb-Sn, Pb-Sb and Pb-Sn-Sb alloy systems and provided an improvement to the resolution for the freckling prediction with respect to the Rayleigh number criterions reviewed, but a critical Rayleigh number value could not be defined because of overlapping of various experimental observations. In a subsequent work, Yang *et al.* extended their form to include the effect of the slope of the solidification front and performed horizontal solidification experiments for verification.¹⁴ The modified criterion form had the weakness that the formulation included the angle that the velocity vector formed with the isotherms, which is not known *a priori*, and makes it difficult to establish an accurate prediction of freckling.

Auburtin *et al.* evaluated the influence of the orientation of the solidification front with respect to the gravity vector.⁷⁸ To include this geometrical effect, they modified the form originally proposed by Sarazin and Hellawell⁸⁴ by replacing the characteristic length with an expression including the permeability of the mushy zone. The modified criterion obtained is presented in equation [2.28], where D_t is the thermal diffusivity, λ_l is the primary dendrite arm spacing and K is the permeability in the vertical direction, which is related to the tilt angle α of the solidification front with respect to the horizontal plane, and the parallel (K_Y) and perpendicular (K_X) components of the permeability by the following equation [2.29]. The formulation of K was originally presented by Scheidegger defining the directional permeability of anisotropic porous media in two-dimensional case.⁸⁵

$$Ra = \frac{g \cdot \frac{\partial \rho}{\partial z}}{\nu \cdot D_t} \cdot \left[\lambda_l \left(\frac{K}{K_Y} \right) \right]^4 \quad [2.28]$$

$$K = \frac{1}{\frac{\sin^2 \alpha}{K_X} + \frac{\cos^2 \alpha}{K_Y}} \quad [2.29]$$

Experiments were performed using a directional solidification furnace with the capacity of inducing a tilted solidification front forming an angle between 0 deg and 35 deg with the horizontal, permitting an evaluation of the proposed form. Their Rayleigh number criterion provided a good resolution in the prediction of freckling for the experimental results. However, their criterion shows a monotonically increasing trend with increasing the tilt angle, although the flow driving force should decrease at high tilt angles.

The critical Rayleigh number values for the different alloys were in a range between 0.65 and 0.95. The deviation from unity was attributed to secondary features of the dendrite morphology.⁸⁶

2.8 Laboratory Scale Freckles Produced during Nearly Horizontal Directional Solidification

Most of the research work reported in the literature involving experiments with laboratory production of freckles and evaluation of predictions for their formation, use analog systems with upward directional solidification^{81, 77, 79}. Experiments inducing freckle channels during horizontal directional solidification of Ni-base superalloys, that resemble the solidification conditions in the mush of VAR ingots are scarce and in most cases use similar experimental arrangements and methodology.^{14, 74, 75} Basically, the experiments seldom reported involve melting the superalloy on a separate induction furnace and pouring the melt into a properly preheated high purity alumina rectangular crucible (~200 mm high x 140~180 mm long x 50 mm thick). A cooling system is then turn on, so a constant low temperature is slowly reached and maintained in one of the vertical surfaces (chill) while the rest of the crucible walls and bottom are maintained at a constant high temperature (above liquidus) by use of active heating. This way, the solidification occurs with directional columnar dendritic growth at overall low cooling rates, and the primary dendrites growth direction in the mush forms an acute angle with respect to the gravity acceleration vector. The solidified slabs are then sectioned for macroscopic metallographic analysis. First the slabs are cut through horizontal planes to detect the cross sections of potential freckle channels formed, and if that is the case, the slabs are carefully sliced through vertical longitudinal planes to provide side views of the channels after some grinding and polishing (like the ones presented in Fig. 2.3). Fig. 2.10 shows a schematic representation of the typical experimental setup.

Fig. 2.10-Experimental setup furnace for near horizontal directional solidification¹⁴

2.9 Prevention of Thermosolutal Convection

Industrial practice has gained a certain degree of maturity in the production of VAR ingots with diameters up to 32 in. Unique cases have been reported where the production

of ingots with diameter up to 36 in. has been successful⁸, but certainly are not the norm at the current state of the processing. To avoid the evolution of macrosegregation defects on the larger ingots, the foundry engineers rely on maintaining process parameters within tight ranges and strict quality control through automation and normalized procedures. Basically, to produce an ingot without incidence of macrosegregation defects it is required to keep constant key parameters: current, voltage, arc length and melting rate, which result in steady heat transfer, steady magneto-hydrodynamics processes and consequently unperturbed steady solidification. X. Wang recently evaluated the effect of processing parameters of VAR on freckle formation by remelting an ingot with variable diameter and variations in the arc gap (changes in current density)⁹. Freckles were formed in the center and midradius of the ingot due to those variations, and these reported results exemplify the fact that as a consequence of the characteristics of the direct current arc process, the key parameters are interrelated and highly dependent on the dimensional quality of the process.

Fig.2.11-Schematic view of a VAR furnace⁷¹

In general shallow molten metal pools, corresponding with low melting rates are known to decrease the probability for macrosegregation defects like freckles, but at the same time, shallow pools increase the occurrence of white spots, so superalloy melt shop engineers end up with narrow ranges for the melting rate. Special control of the composition and geometry of the electrode are fundamental to maintain an even distribution of the arc and assure a well distributed heat transfer between the electrode and the molten pool. Strong and stray magnetic fields need to be controlled in order to prevent variations in the symmetry of the current and hence variations on the electrode surface and the shape of the molten metal pool. Excellent accuracy in alignment of the electrode and high speed control of the positioning assures a constant arc gap and annulus (tubular space between the electrode and the copper crucible in Fig. 2.11), resulting in

constant current and prevention of preferential melting and side arching. In particular, side arching could lead to catastrophic failure if not controlled on time.

The scale of the installed VAR process equipment make improbable the use of alternative ways to block the formation of defects like precession or rotation to halt the evolution of channeling, and hence on freckles formation, as it has been successfully done on the small experimental apparatus. A typical VAR ingot is several meters long and weight more than 20 Tonnes. In general, it is difficult to implement external forces to affect the fluid dynamics occurring on the mush in order to control the macrosegregation patterns. Nevertheless, the current distribution inside the molten pool is not known with accuracy, and it has been shown that the convection in the bulk molten metal highly depends on the competing effects of the natural thermal convection and the Lorentz forces and it is highly probable that these convection patterns affect the nucleation and growth of freckles. From the academic point of view, contributions to prevention of the macrosegregation focus on further refinement of the gained understanding of the mechanisms and development of tools to provide conceptual support to tradeoffs on the regulating aspects like the thermal conditions at the solidification front and chemical composition of the alloys. Common lines of interest include decreasing the driving force and increasing the impedance to the interdendritic liquid flow.^{87, 88} For reduction of the driving force, the methodology relies on systematic alloy design; by including controlled additions of alloying solute elements that may help control the density change of the interdendritic liquid by directly contributing on the final density or by forming secondary phases which become irrelevant on the interdendritic density change like high melting point carbides. Meanwhile, increasing the impedance to the convective flow has been pursued by including additions of chemical elements that promote the precipitation of secondary phases that may act as drag enhancers on the mush. Also, further understanding of the microscopic phenomena and how to incorporate the relevant effects to macroscopic models is receiving considerable attention, particularly with the promising advances in new methodologies like the phase field theory or the cellular automata technique^{89, 90}.

All the improvements in the process that have already been obtained so far cannot totally prevent macrosegregation and in particular, freckles formation. Besides, the tendency of increasing the diameter of VAR ingots is steady, as emerging technologies in power generation are demanding increased yields of high quality superalloy ingots. The new challenges make necessary to focus on the fundamental mechanisms of formation of macrosegregation for effective prevention. A clear evidence of this need is that about 12 percent of the articles presented in the latest International Symposium on Liquid Metal Processing and Casting, held in September 2009, were related to optimization of processing aiming to prevent macrosegregation defects.

3. METHODOLOGY

As reviewed in chapter two, the macrosegregation defects that develop during solidification in the VAR processing are known to be consequences of thermo-solutal convection occurring in the bulk liquid and the mushy layer. Considering that these defects have a common origin, the research work presented here focused in the prevention of freckles, with the confidence that advances in their prevention will also be valuable and feasible for other defect patterns. The evolution of the convection flow in the mush layer can be interpreted as the departure from the balanced condition on which the driving forces are counteracted by the resistance imposed by the dendritic array. Improved physical interpretation of the mechanism of freckling in VAR ingots and more accurate experimental data related to the magnitudes of the interacting forces are essential toward the final goal of preventing macrosegregation. With respect to the impedance or resistive force, the main parameters are the viscosity of the molten metal and the permeability of the partially solidified mush layer. Their experimental determination implies great difficulties, because of the high temperatures required (1300 C ~ 1450 C). In regard to the driving force, density measurements of the molten liquid are difficult for the same reason, and scientists need to rely on theoretical assumptions to determine the density gradient in the mush layer. The approach adopted in this research was to make a contribution on the estimation of the driving force, by means of obtaining accurate data useful to determine the density gradient, and proposing a criterion for freckling prediction with an improved resolution to discern between the conditions of ‘Freckle – No freckle formation’. Consequently, the conceived experimental tasks included two stages of experiments. The first stage conceived the measurement of the partition coefficients of the major strengthening alloying elements with verification supported by thermodynamical calculations through cooperation with researchers at the Phases Research Lab at Penn State University. This cooperative effort is very valuable because complements the contribution of Sung and Poirier⁹¹ by covering a different alloy system, towards the final goal of constructing an extense index of measured partition coefficients which can be used to refine the databases that support the thermodynamic calculations used in computational modeling and prediction of solidification macroscopic defects. The second stage envisioned the verification of the proposed freckle criterion by confronting its performance for freckle prediction against experimental data of horizontal directional solidification. This chapter aims to provide a general description of the methods followed while addressing the impact of the important variables and decisions over the outcome of this research. Certainly, further details of the methodology are included in the presentation and analysis of the experimental results.

3.1 Experimental Determination of the Partition Coefficients of Major Solute Elements on Simplified Ni-Base Superalloys

3.1.1 Model Alloys Preparation

Because the Ni-based superalloys of interest in this research contain various alloying elements, (see table 3.1) a systematic approach was required to isolate the different

effects obtained by these additions. Therefore, simplified model alloys were produced with varying major alloying elements including the strengthening solute elements within the ranges found on commercial superalloys. The complete set of nominal alloys designed is presented in table 3.2. The model alloys were produced following a process that started by adding the appropriate amounts of pure metals and compressing the mixture of powder and fragments with a manual hydraulic press. Weighting of the components was performed using an analytical scale with 0.001 g resolution and the conformed wafers were melted using a tri-arc button furnace.

Table 3.1 Chemical compositions of the commercial alloys of interests (wt%)

Alloy	Ni	Co	Cr	Fe	Nb	Mo	Ti	Al	C	Si
IN-718	53.62	0	18.19	17.77	5.41	3.01	0.98	0.56	0.04	0.03
IN-706	41.39	0.03	16.3	37.03	2.98	0.12	1.7	0.19	0.01	0

Table 3.2 Chemical compositions of the model alloys designed (wt%)

Alloy ID	Specific	Cr	Fe	Nb	Al	Ti
1	Ni-Cr-Nb	15		3		
2		15		4.5		
3		15		6		
4		20		3		
5		20		4.5		
6		20		6		
7	Ni-Fe-Nb		5	3		
8			5	5		
9			10	3		
10			10	5		
11			18	3		
12			18	5		
13			36	3		
14			36	5		
15	Ni-Cr-Fe-Nb	18	10	3		
16		20	18	3		
17		18	18	5		
18		20	10	5		
19	Ni-Cr-Al	15			0.6	
20		20			0.6	
21		18			1.0	
22		20			1.5	
23	Ni-Cr-Fe-Al	15	10		0.6	
24		20	10		0.6	
25		15	20		1.0	
26		20	20		0.6	
27	Ni-Cr-Ti	15				0.5
28		15				1.5
29		20				0.5
30		20				1.5

Careful cleaning of the furnace chamber interior was executed between charges followed by various cycles of vacuum/pressure of ultra high purity Argon to flush the air inside the chamber. A liquid Nitrogen cold trap was installed in the vacuum line to eliminate carbon contamination due to back streaming of pump oil vapor⁹². All melting steps were conducted under an ultra high purity Argon atmosphere at a gage pressure of about 2 psi to avoid any potential leaking of air into the chamber, and Titanium strips were located inside the chamber, near to the high temperature zone, to induce selective oxidizing, and protecting the sample material during the arc melting. To obtain homogeneity, each solidified button was remelted at least three times, turning it upside down between melts. Two different buttons of approximately 2 g were prepared for each model alloy (independent repetitions), aiming to decrease the effect over the final composition of the experimental errors related to the weightings of the raw materials and to the possible partial mixing during the melting steps. All melting-solidification cycles were finished by inducing a vast flow of ultra high purity Argon in order to induce a very fast cooling of the solidified buttons. Usually, the buttons reached room temperature at approximately 10 minutes after the arc was turn off.

Fig. 3.1- Centorr Model 5TA Reed Tri-Arc Furnace with water cooled resistor bank, electrodes head and heart.

Fig. 3.2 – Model alloys preparation steps. (1) Raw materials (2) Conformed waffle (3) Before melting with Ti piece for Oxygen capture (4) Button solidified

It was found that some fragments extracted from the produced buttons had the existence of discrete spots with uneven compositions related to partial mixing, although the provisions taken to provide good mixing. All samples with those inhomogeneities were rejected and were produced again. To be on the safe side, additional buttons were added to all compositions in order to increase the number of fragments with the appropriate composition distribution for the rest of the experimental process. The nearly doubled work load for the processes of melting, cutting, and metallographic preparation for Scanning Electron Microscopy /Energy-Dispersive X-ray (SEM/EDS) analysis, was alleviated by involving the support of a student monitor from the Mechanical and Aerospace Engineering Department at WVU. The increase amount of material also permitted to ensure an improved randomness of the error inherent to experimental procedures. Fig. 3.1 shows the Centorr Model 5TA Reed Tri-Arc Furnace⁹³ used, while Fig. 3.2 schematically shows the steps followed for buttons preparation.

3.1.2 Differential Thermal Analysis (DTA) Procedure

The model alloy samples were sectioned with diamond saw to prepare specimens with sizes between 80 and 250 mg for regular DTA and quenching Modified DTA experiments (MDTA). Larger fragments were kept for SEM/EDS analysis of the fast cooled as-cast condition.

High purity Al_2O_3 powder and cups were used as reference material and crucibles respectively, and the atmosphere was controlled by maintaining ultra high purity Argon flow at $2 \text{ cm}^3 \text{ s}^{-1}$ for all DTA runs (calibration and regular DTA). Sample thermocouple calibration was performed using the melting point temperature of Silver (99.99 wt %) and Nickel (99.99 wt %) standards, at a rate of 0.17 K s^{-1} . For the calibration, the onset temperature of melting was determined on the heating cycle by using the method of extrapolation, described by Boettinger and Kattner⁹⁴, on which the onset temperature is taken as the intersection between the forward extrapolated baseline of the DTA curve (ΔT vs T) right before melting onset, and the linear asymptote of the DTA curve just after the melting onset, corresponding to the negative slope segment of the downward endothermic peak.

By the calibration of the DTA instrument using melting signals of the pure metal standards (Ag, Ni) it was assured that the effect of the characteristic time responses of the heat transfer flow within the instrument and the heating rate effect would not affect the measurements⁹⁴, and that the possible differences between the measured transition temperatures and the real phase boundaries temperatures were mostly related to the compositional heterogeneity of the rapidly cooled as-cast samples⁹⁵. The DTA experiments were performed using heating and cooling rates identical to the ones used on the calibration runs, i.e., of 0.17 K s^{-1} for regular DTA experiments. The incipient melting temperature value was determined on the heating cycle as the onset melting temperature measured by using the method of extrapolation, while the liquidus temperature was determined by the maximum of the endothermic peak also during heating^{95,96}. All DTA experiments were performed at least three times for each specimen, two different

specimens were used per model alloy composition and the corresponding sets of data were averaged.

3.1.3 Modified Differential Thermal Analysis (MDTA) Procedure

After the regular DTA experiments were performed, the thermocouples assembly of the standard differential scanning calorimeter was replaced by a modified assembly that permitted placing a quenching bath inside the alumina tube furnace. Fig. 3.3 shows a photograph of the thermocouple assembly with the oil pool in the bottom region. In Fig. 3.3, a sample with solidified semi-spherical shape lies on top of an alumina rod. The alumina rod functioned to contain the sample and reference thermocouples.

Fig. 3.3 – Modified thermocouples assembly with quenching bath (alumina tube furnace removed)

Recalibration runs were performed using the modified thermocouples assembly at heating/cooling rates of 0.083 Ks^{-1} to facilitate the quenching step. Because the sample and reference thermocouples were both affected by the latent heat evolved on melting and solidification reactions, the incipient melting temperature and the liquidus temperature were tracked by the change of slope with respect to the local baseline on the modified DTA curves, and the method of extrapolation explained above was used for both transition temperatures. Fig. 3.4 shows an example of the typical curve observed by using the modified thermocouples assembly.

In all MDTA experiments, the temperature was further increased to 60 K above the observed change of slope of the local baseline during the heating step corresponding to the liquidus temperature, and an isothermal dwell was subsequently applied to permit homogenization on the liquid state. During the cooling cycle, the specimen was tapped to fall in the quenching bath shortly after detecting the change of slope of the local baseline corresponding to the start of the solidification. As undercooling was observed, the solid fraction at the quenching temperature was determined by metallographic analysis of the

quenched samples. Commercial Alloy IN718 samples were also included in the set of quenching DTA experiments to compare the results obtained with the methods used in this work and the reported values in the literature. In the first trials, some samples in the partially solidified state adhered to the alumina rod and the tapping of the sample for quenching was unsuccessful. Recalibrations were required to include a separator thin disc, cut from a failed alumina rod, which acted as a tray to hold the mushy sample. The tapping of the disk-sample couple was then successful and adopted in the rest of experiments. Recalibrations were required when the disc could not be separated from the quenched sample or was broken due to quenching and needed to be replaced. Also, it is important to mention that the technique required training because sometimes the tapping step was not fast enough so the sample was completely solidified before falling to the quenching oil or the shear movement was excessive and the sample ended stock to the inner surface of the alumina tube furnace.

Fig. 3.4 –Temperature vs Temperature difference DTA curve for quenching experiments

3.1.4 Metallographic Procedure

The quenched samples and the fast cooling as-cast fragments were prepared for optical and SEM/EDS. Conventional grinding and polishing steps followed by ultrasonic cleaning were included for all samples. No chemical etching was used for the samples to be analyzed by SEM. EDS was performed for the fast cooling as-cast samples over large areas to keep track of the overall composition. For the quenched samples the EDS data was also collected over areas which were adjusted to include only primary dendrites or eutectic constituent. Careful selection of the primary dendrite areas and eutectic constituent areas was used in order to best resemble the compositions near the boundary solid/liquid before quenching. EDS from points (spots) was limited to the analysis over arbitrary lines across dendrite stems. EDS analysis was carried out in the standardless mode with acceleration voltage of 20 kV, take-off angle of 35 degrees and, when applicable, spot size of about 2 μm .

3.2 Experimental Verification of the Freckling Criterion Proposed

High temperature directional solidification experiments are complex and require efficient transformation of great amounts of energy in form of electrical power into heat. Quality assurance of all materials and procedures used is fundamental for the integrity of the equipment and hence, decisive for safe operation. Type B thermocouples (Pt30%Rh vs Pt/6%Rh) are required for control and temperature data collection, high purity ceramic materials and special heating elements, make the equipment and the associated experimental tests very expensive.

3.2.1 Materials

The main goals for the directional solidification experiments were to create freckles at laboratory scale using model alloys from the set designed in this project and to test the performance of the proposed criterion for freckling. The materials were produced as ingots of 4 in. diameter x 14 in. length and obtained by donation from Special Metals Corporation (Huntington, WV). The compositions from the set of model alloys intended to evaluate the freckling prediction criterion were chosen by the considerations that follow, and the obtained compositions of the ingots are presented in the table 3.3.

Nb Content:

The chemical composition is essentially chosen to facilitate the freckles formation. The amount of Nb was as high as possible because the freckling potential is higher at the solubility limit of Nb in proeutectic gamma phase, but to maintain similarity with commercial alloys, Nb content was set at 6 wt%. The amount of Chromium was aimed at 15 and 20 wt%. The final model alloys of the ternary system Ni-Cr-Nb are:

Ni-15Cr-6Nb : (DS1)

Ni-20Cr-6Nb : (DS2)

The alloy with composition code DS1 will serve to corroborate the behavior observed in a previous research work on which the decrease of Nb from 8.6 Wt. % to 6 Wt. % greatly changed the freckling potential⁹⁷. The proposed experiments including this experimental point will provide further experimental verification on the matter.

Al Content:

W. Yang *et al.*⁹⁸ measured the Aluminum initial partition coefficient to be 1.05 while in this work the value was found to be between 1.11 and 1.21 (see chapter 4). Being the Aluminum a lighter element, its preferential partition to the solid is expected to make the interdendritic liquid heavier than the bulk liquid, adding a freckling tendency to the segregation of heavy Niobium. Considering this, the aluminum will be selected in the high level studied in the model alloys, with a value of 1.5 wt. % to permit direct comparison of its effect with respect to the same addition of Ti on a Ni-Cr-Fe base.

Ni-20Cr-10Fe-1.5Al: (DS3)

Ti content:

The partition coefficient of Ti was measured in commercial alloy IN-718 by Wanhong Yang et al⁹⁸. and found its magnitude to be approximately 0.59. The microsegregation of Ti makes the interdendritic liquid lighter, and freckle formation in Ti-containing alloys was observed for model alloys under horizontal directional solidification. The model alloy selected will have the higher level of Titanium studied on the DTA experiments.

Ni-20Cr-10Fe-1.5Ti: (DS4)

Table 3.3 Compositions of the ingots obtained fro directional solidification tests

HEAT	HV1281	HV1282	HV1283A	HV1284
C	0.024	0.032	0.024	0.012
MN	0.003	0.009	0	0
FE	0.0399	0.0453	10.08	10.08
S	0.00067	0.0011	0.00122	0.00122
SI	0.048	0.069	0	0
CU	0.0318	0.0335	0.0029	0.011
NI	78.099	73.523	67.975	68.328
CR	15.47	19.91	20.29	19.95
AL	0.145	0.155	1.51	0.136
TI	0.0347	0.0382	0.0619	1.438
MG	0	0	0	0
CO	0.0275	0.0264	0	0
MO	0.0099	0.0093	0.0052	0
NB	6.02	6.088	0	0.0147
TA	0.012	0.017	0.003	0.008
P	0.0024	0.0028	0	0.0002
B	0	0	0	
CA	0.0003	0.0003	0.0009	
V	0.0055	0.0072	0.0164	0.0052
W	0	0.0039	0.0054	0
ZR	0	0	0	0

3.2.2 Directional Solidification (DS) Furnace

The directional solidification furnace used consists of a cylindrical high purity alumina retort tube closed in one end, than has controlled internal atmosphere (High purity Argon) and is heated by radiation at the outer surface. The furnace is radially isolated and heated by 6 molybdenum disilicide elements located in two rows, each side of the retort alumina tube as shown in the pan view on Fig. 3.4. The heating units can withstand a maximum temperature of 1700 °C (heat sources Q1, Q2, Q3) in air. The design of the furnace permitted adjusting the temperature in three different zones independently, along the longitudinal direction for a given time (labeled as 1, 2, and 3 in Fig.3.4). By proper adjustments, it was possible to induce a given cooling rate maintaining a constant temperature gradient along the alumina tray containing the sample material. The heat flow was mainly unidirectional and induced from the ‘open end’ of the retort tube by means of a water cooling system (Q4). The required special electrical distribution circuit

was installed in the room where the experimental set up is located, and the furnace controlling unit was updated by incorporating retransmission modules to each zone. Temperatures could then be monitored and the heating/cooling curves could be stored using a data acquisition system on a dedicated PC. To assist the process, and correlate the control measured temperatures outside the retort tube with the internal temperature near the crucible, a special custom made Type B thermocouple was installed along the axis of the furnace (y-axis) so the measuring junction was located just above of the crucible to monitor the temperature near the top surface of the molten metal during the experiment. The freedom of controlling independently the different zones of the furnace, although advantageous, required special attention to the programmed heating cooling trajectories. It is essential that the different cycles of heating and cooling in the different zones will not induce rates greater than 150 C/min since the retort tube could fail due to thermally induced stresses. Not as critical, is the gradient along the tube at a given time, which actually withstands gradients of about 2.5 C/mm.

Fig.3.4 -DS furnace. Tray crucible and control thermocouples per zone included.

3.2.3 Experimental Plan

The experimental plan included two parameters or control variables, which were the chemical composition of the alloys and the cooling rate at a constant gradient (therefore the growth rate). The chemical composition should vary within four different levels as defined above, while the cooling rate varies between two levels. Eight different configurations for DS experiments would be included. The levels of variation for the cooling rates were determined by previous results on directional experiments performed by Chang and co-workers⁹⁷. Preliminary exploration runs were performed to fine tune the heating/cooling cycles for each zone of the furnace, to attain the cooling rates throughout the molten liquid. At least three repetitions of the definitive experiments were planned to be performed for each of the eight different configurations presented in Table 3.5. The experimental design considered the existence of freckles as response variable (output variable).

Table 3.5. Experimental matrix proposed

Composition	Cooling rate: low (r)	Cooling rate: high (R)
	3 C/min	9 C/min
DS1:a	ar	aR
DS2:b	br	bR
DS3:c	cr	cR
DS4:d	dr	dR

4. EXPERIMENTAL INVESTIGATION OF PARTITION COEFFICIENTS OF SOLUTE ELEMENTS WITH THERMODYNAMIC CALCULATION VERIFICATION

In the following section the most important results obtained on the experimental determination of the partition coefficients via quenching Modified DTA (MDTA) with verification by thermodynamical calculation are presented. The ternary alloy systems Ni-Cr-Nb and Ni-Fe-Nb are used to illustrate methodological details that were applied for all the alloy systems. Additional results are included in appendices C to E.

4.1 Model Alloy Samples Production and Regular DTA Tests

The target and obtained chemical composition ranges and averages for the subsystem Ni-Cr-Nb are presented in table 4.1. Besides the listed elements, some Carbon was detected, but its small quantity was not determined due to limitations on the resolution of the EDS analysis. The microstructures obtained on the as-cast condition after metallographic polishing revealed almost featureless surfaces of gamma grains with some presence of globular carbides. No other secondary phases were detected, and in the case of the alloys from the system Ni-Cr-Nb, this result was expected due to the composition and the thermal history of the samples. The absence of γ' is likely related to the lack of alloying elements like Al and Ti, and the fast cooling of the as-cast buttons should have prevented the precipitation of γ' which is diffusion controlled. (Appendix C includes the composition ranges and averages for the rest of alloy systems).

Table 4.1 Chemical composition of model alloys produced system Ni-Cr-Nb [Wt. %]
(Balance Ni)

Alloy ID (target)		Nb	Cr
Alloy 1 (Ni-3Nb-15Cr)	Min.	1.79	14.14
	Max.	3.15	14.94
	Aver.	2.62	13.54
Alloy 2 (Ni-4.5Nb-15Cr)	Min.	3.49	11.39
	Max.	4.57	21.8
	Aver.	3.95	15.6
Alloy 3 (Ni-6.0Nb-15Cr)	Min.	5.57	8.18
	Max.	6.75	18.17
	Aver.	6.32	12.5
Alloy 4 (Ni-3Nb-20Cr)	Min.	2.47	16.81
	Max.	3.66	17.08
	Aver.	2.94	17.50
Alloy 5 (Ni-4.5Nb-20Cr)	Min.	4.38	14.95
	Max.	5.15	19.59
	Aver.	4.76	17.86
Alloy 6 (Ni-6.0Nb-20Cr)	Min.	5.50	17.80
	Max.	6.03	18.11
	Aver.	5.75	17.98

Although careful calibration procedures were used, the DTA measurements showed noticeable differences with respect to the theoretically calculated values. These differences can be considered to have both contributions, from the experimental procedures and from the theoretical calculations. The compositional heterogeneity of the fast cooled as-cast samples and the smearing of the latent heat of fusion during the pure metal standards melting are recognized as the most important factors inducing uncertainties to the DTA experimental results. Solute incomplete mixing on the as-cast samples and heat flow smearing the evolution of latent heat of fusion of the calibration materials, (which builds a wider difference between the sample thermocouple junction and the real sample temperature), might be the key factors for variability in the incipient melting and liquidus temperatures⁹⁹. Nevertheless, the DTA measurements performed in this work had the specific objective of complementing the equilibrium theoretical values in the determination of the approximate mushy zone range of the model alloys, by including the effect of the instrument response and giving a reference about the extend of undercooling to expect for the MDTA experiments.

In Fig. 4.1 a pair of curves forming a band are included, which correspond to the solidification paths calculated using the equilibrium method with the ThermoCalc™ Ni database (Ni7), for the minimum and maximum alloying content compositions found for the same target model alloy (Alloy 5). It was observed in almost all samples that the solidus temperature registered in the DTA tests presented a higher variability with respect to the liquidus temperature. This is a typical result also found in experiments with other metallic alloy systems like steel,¹⁰⁰ and the decreasing spread of the data for the liquidus measurements with respect to the corresponding solidus have been attributed to the radiation effect of equalizing the temperature within the sample holder assembly¹⁰¹ at higher temperatures.

Fig. 4.1-Experimental temperatures vs theoretical calculations, using equilibrium method and commercial Ni database

In spite of the fact that there is always variability on the experimentally determined solidus and liquidus temperatures, two overall tendencies were observed in this work for the system Ni-Cr-Nb, and virtually for all the systems studied: (1) the transition temperatures were consistently found to be higher than the values obtained by

ThermoCalc™, and (2) the effect of increasing amounts of solute elements depressed the measured temperatures.

4.2 Experimental Results and Comparisons

4.2.1 Areal EDS Analysis

For the Ni-C-Nb system, the SEM analysis of the quenched samples showed that the interdendritic liquid in the mushy zone transformed involving two different eutectic reactions. Meanwhile, no precipitation of secondary phases was found on the primary dendrites. The fast quenching step and the observed absence of precipitates ostensibly lowered the possibility of spot EDS compositional measurement scattering induced by the presence of undetected particles with a size comparable to the X-ray interaction volume. However, since in all experimental EDS measurements exists the chance of skewed or biased averaging process, preventive actions were taken as recommended in the literature¹⁰². The fast cooling on the quenching step induced the formation of eutectic constituents with fine lamellae, with sizes of the order Knorovsky *et al*¹⁰³ indicated to be appropriate for obtaining a representative averaged composition of the parent liquid from areal data collected over the interdendritic eutectic regions. One eutectic reaction mainly occurred when the amount of Niobium was in the lower level and the eutectic phases formed were gamma and Laves. This type of eutectic constituent presented an average composition in weight percent of 66.82 Ni – 11.60 Cr – 21.6 Nb and the scanned area is highlighted in Fig. 4.4 between the secondary arms of the proeutectic gamma dendrites. The other eutectic reaction occurring, had gamma and NbC as product phases, and its morphology was the same as the eutectic observed by DuPont *et al*¹⁰⁴. The averaged composition in weight percent of this eutectic constituent was 71.67 Ni – 15.23 Cr – 13.09 Nb and a typical scanned area is highlighted in Fig. 4.5. The tendency of formation of eutectic NbC was related to the higher level of Niobium for constant amount of Chromium. The model alloys with the intermediate level of Niobium, presented a mix of phases corresponding to both eutectic reactions. Fig. 4.6 shows secondary arms of proeutectic gamma dendrites with NbC with a shape known as “Chinese script”. In the same figure, the gamma/Laves eutectic regions have a shape that contours the already formed solid phases, evidencing that the associated eutectic reaction was the last step in the solidification path as reported in the literature.

Fig. 4.4-Gamma/Laves eutectic between proeutectic gamma dendrites (Low Nb)

Fig. 4.5-Gamma/NbC eutectic between proeutectic gamma dendrites (High Nb)

Fig. 4.6-Gamma/NbC/Laves eutectic mix between proeutectic gamma dendrites (intermediate Nb)

During the SEM/EDS analysis of the quenched samples, composition data was collected from many areas containing only proeutectic dendritic gamma. The total set of collected data was then averaged to obtain the i -th solute element amount in the solid as C_{dend}^i . On the other hand, to represent the composition of the samples in the complete liquid state C_0 , average values were obtained for each model alloy from the as-cast composition measurements. The average partition coefficients for Nb and Cr were calculated by the ratio C_{dend}^i / C_0 . The results obtained for the samples with the extreme variation levels of solutes are presented in Table 4.2. By comparing the results of rows one and two, the effect of increasing Cr content from 15 to 20 Wt. % with approximately constant low level of Nb was to slightly decrease the partition coefficients. The same effect of increasing Cr over the partition coefficients was observed for the alloys with higher Nb content when comparing rows three and four. Meanwhile, the effect of increasing the amount of Nb on the average partition coefficients can be studied by comparing rows one and three for the low level of Cr, and rows two and four for the high Cr level. In both cases, the increase in Nb from 3 to 6 Wt. % increased both average partition coefficients.

Table 4.2- Average and Scheil fitting partition coefficients of solute elements in Ni-Cr-Nb system

Model Alloys	$K'_i = (C_{\text{dend}} / C_0)$		(Scheil fitting)	
	K'_{Nb}	K'_{Cr}	K_{Nb}	K_{Cr}
Ni -15.4Cr -3.0Nb	0.554	0.932	0.530	1.017
Ni -19.0Cr -3.1Nb	0.501	0.795	0.435	0.846
Ni -13.4Cr -6.3Nb	0.607	1.105	0.630	1.080
Ni -17.9Cr -5.75Nb	0.592	1.017	0.555	1.042

Eutectic products observed in the system Ni-Fe-Nb were gamma and μ phase (Nb_7Ni_6), as predicted by the thermodynamic calculations performed with the newly developed database¹⁰⁵. Fig. 4.7 shows an example of the microstructure obtained.

Fig. 4.7-Gamma/ Nb_7Ni_6 eutectic between proeutectic gamma dendrites (Ni-5Fe-3Nb)

Table 4.3 shows the partition coefficients of Nb and Fe for the Ni-Fe-Nb system. Model alloys included correspond to the target extreme levels of variation. The method described above was used for the two first rows, while the values obtained for the model

alloys in rows three and four were obtained by the method of point fitting explained in the next section.

Table 4.3. Summary of the measurements of the partition coefficients of Nb and Fe

Model Alloys	Method	K_{Nb}	K_{Fe}
Ni -5 Fe -3Nb	$K'_i = (C_{dend} / C_0)$ (Average)	0.52	1.03
Ni -36Fe -3Nb		0.30	1.59
Ni -5Fe -5Nb	Scheil Fitting	0.63	1.05
Ni -36Fe -5Nb		0.29	1.05

4.2.2 Point EDS Analysis

The second methodology used for the determination of the partition coefficients of the solute elements in the quenched model alloys was based on SEM/EDS point measurements over arbitrary lines across the primary dendrites. Point measurements obtained from interdendritic areas were discarded for the segregation profile fitting as pointed out in the technique used by Gungor.¹⁰⁶ According to the segregation tendency and following the methodology proposed by Flemings *et al.*¹⁰⁷ the data was ranked and assigned an apparent solid fraction from almost zero (to make up for the low probability that the cutting plane of analysis actually contained the core of the dendrite arm), to the maximum solid fraction reached before quenching. The solid fraction reached before quenching could not be deduced from the quenching temperature due to undercooling effects, hence, the maximum apparent solid fraction reached before quenching was determined by areal measurement using Hillard's quantitative metallography analysis.¹⁰⁸

Considering that cooling stage for the modified DTA experiments was initiated with slow rate (0,083 Ks⁻¹) before inducing the quenching, it was reasonable to suppose local equilibrium was maintained at the interface solid-liquid during the solidification, *i.e.* there was no significant supercooling of the dendrite tips, and the nonequilibrium lever rule was still applicable.¹⁰⁹ The Scheil supposition was adopted, assuming no back diffusion to the solid and complete mixing of the solute elements in the liquid. The partition coefficients were obtained by fitting the segregation profiles found on the proeutectic gamma dendrites to the Scheil equation¹¹⁰ (equation 2.2).

For every solute element measured composition C^* , a component of the squared error vector was defined according to equation [4.1]. The summation of the squared error for all measurements was then minimized with respect to the partition coefficient, using a simple code written in Matlab©¹¹¹ which is included as appendix D. This method constitutes an alternative aiming to avoid potential subjective misjudgment in the detection of differences between the theoretical curves and the experimental data profiles as described by S. Tin *et al.*¹¹²

$$error = (C^* - C_s)^2 = (C^* - kC_0(1 - f_s)^{k-1})^2 \quad [4.1]$$

Fig. 4.8 and 4.9 present the error of fitting to the Scheil equation as a function of the partition coefficient of Nb for the quenched samples of model alloys 1 and 4 respectively.

It is observed that the value of 0.530 for the partition coefficient of Niobium best fits the experimental data to the Scheil equation for the low level of Cr present (15 Wt %), while the fitting error to the Scheil equation was minimized when the partition coefficient of Nb was 0.435 for the higher level of Cr (20 Wt %). Although the magnitudes for the partition coefficients were slightly different between the two experimental measurement methodologies, presented in Table 4.2, the results obtained for the effect of Cr and Nb on the partition coefficients by the profile fitting method were in good agreement with the tendency found for the average partition coefficients and with the predicted tendencies that will be presented later in the theoretical simulations. Additional results for the method of Scheil fitting are included in appendix E.

Fig. 4.8-Fitting error to Scheil equation vs partition coefficient of Nb for Ni-3Nb-15Cr

Fig. 4.9-Fitting error to Scheil equation vs partition coefficient of Nb for Ni-3Nb-20Cr

4.2.3 Validation with Commercial Alloy 718

In order to verify the validity of the new methodology proposed for the analysis of the model alloys, the commercial superalloy 718 was included in the DTA and MDTA tests. The partition coefficients of the alloying elements in alloy 718 also were determined using the profile fitting method. Fig. 4.10 shows an example of the DTA thermograms

obtained for the alloy 718 samples, where the transition temperatures in the heating cycle are identified, and includes (in parenthesis) the data reported by W.D. Cao *et al.*¹¹³ Fig. 4.11 shows a secondary electrons SEM image obtained from the sample of alloy 718 solidified at a rate of 0.17 Ks^{-1} in the regular DTA tests. The phases are identified as shown, while in Fig. 4.12 the quenched structure for a sample of the same commercial alloy is presented. The eutectic reaction products were gamma and laves phase. The methodology of profile fitting to the Scheil equation was used for the quenched samples of alloy 718, and the partition coefficients for the major and strengthening solute elements were determined and are presented in table 4.4 along with reported values in the literature¹¹⁴. The greatest difference was found for the partition coefficient of Ti, which in this work, was found to have a stronger tendency to partition to the proeutectic gamma phase. The agreement between the previously reported experimental data gives reliability to the experimental procedure used in this work.

Fig. 4.10-Thermograph of DTA experiment for IN-718 sample

Fig. 4.11-SEM micrograph of alloy IN-718 sample from regular DTA

Fig. 4.12-SEM micrograph of alloy 718 sample from quenching MDTA

Table 4.4- Partition coefficients calculated using the profile fitting methodology

Partition coefficients for solute elements		
Alloy 718	This work	W. Yang <i>et al.</i> ¹¹⁴
Al	0.8	-
Nb	0.4	0.45
Mo	0.92	0.72
Ti	0.81	0.6
Cr	0.99	1.06
Fe	0.97	1.13

4.3 Thermodynamic Calculation Comparisons with Experimental Partition Coefficients

The measurements of the partition coefficients were compared with predictions made by thermodynamics and kinetic approaches. Different databases were used in the predictions, including the one developed by Du *et al*¹¹⁵ and the ThermoCalc™ Ni database Ni7. The calculations were performed using three different methods: (i) the equilibrium model via the lever rule, (ii) the back diffusion model implemented in the Dictra software, and (iii) the Scheil's model. Further details on the thermodynamic calculations can be found in the literature.¹¹⁶

Fig. 4.13 illustrates the calculated phase transition temperatures and the partition coefficients of Cr and Nb as function of solid fraction in the Ni-15Cr-xNb and Ni-20Cr-xNb (Wt.%) alloys by Dictra simulation. The thermodynamic data are taken from Du *et al*'s results; the cooling rate was set as 0,17 Ks⁻¹. With increasing of Nb and/or Cr content, Fig. 4.13 indicates that the phase transition temperatures decrease.

The contents of elements Nb and Cr have opposite influence on the calculated partition coefficients of Cr and Nb. With increasing of Nb content, the partition coefficients of both Cr and Nb increase for each fixed solid fraction, while with increasing of Cr content the partition coefficients of Cr and Nb decrease. It should be remarked that the equilibrium calculation and the Scheil model will give the same trends as those obtained by Dictra calculation, and also those trends still hold by using the Ni7 database. Further emphasis was preferentially given to the effect of Cr content over the partition coefficient of Nb, given the fact that the effect of Nb content over the Cr partition coefficient does not affect greatly the macrosegregation tendency because the partition coefficient of Cr is very close to unity. Using the Ni7 database and the equilibrium model, the Gibbs energies for the gamma and the liquid phases at a temperature of 1385 C were calculated as a function of the molar Nb content for the alloys of the system Ni-Cr-Nb, with low and high level of Chromium (15 and 20 Wt. % respectively). The common tangent to the Gibbs energy curves of the gamma and liquid phases was analytically calculated for both model alloys. It was accurately confirmed that the theoretical prediction of the increase in the Cr content from 15 to 20 Wt. % decreased the partition coefficient of Nb from 0.469 to 0.3689 (21% reduction). This result supports the experimental findings, and implies that the chance of formation of freckles increases with Cr additions. Figure 4.14 shows the Gibbs energy curves of gamma and liquid phases for alloy Ni-15Cr-3Nb (Wt.%), along with the common tangent traced between the corresponding tangency points, while Figure 4.15 corresponds to the case of alloy Ni-20Cr-3Nb (Wt.%). Table 4.5 presents the Nb molar contents corresponding to the tangency points which define the compositions for the phases to coexist in the mush and the calculated partition coefficient for Nb is included.

Fig. 4.13- Calculated phase-transition temperatures and partition coefficients of Cr and Nb as function of solid fraction in Ni-15Cr-xNb and Ni-20Cr-xNb (wt. %) by DICTRA¹¹⁶

Fig. 4.14- Gibbs energy curves for gamma phase and liquid phase. Common tangent is drawn between the corresponding contact points (alloy Ni-15Cr-3Nb)

Fig. 4.15- Gibbs energy curves for gamma phase and liquid phase. Common tangent is drawn between the corresponding contact points (alloy Ni-20Cr-3Nb)

Table 4.5-Theoretical compositions for gamma and liquid phases in equilibrium in the mushy zone at 1385 C

Alloy	tangency points Nb content in molar fraction		
	Solid phase	Liquid phase	K_{Nb}
Ni-15Cr-Nb	0.015933	0.033918	0.46976
Ni-20Cr-Nb	0.0090403	0.024506	0.3689

Two databases were used to predict the partition coefficients of Fe and Nb in the Ni-Fe-Nb system. Those databases were the TTNi6 Ni-database¹¹⁷ and the recently developed by the partner team at Phases Research Lab at Penn State¹⁰⁵. Fig. 4.16 shows that most of measurements have good agreement with the equilibrium predicted values; however there is a relatively large difference for the partition coefficient of Fe of Ni-36Fe-5Nb. The same trend was observed in Fig. 4.17 when the Scheil model was used. The difference, which remains to be resolved, could be associated to the fact that the solidification on the experiments occurred in global conditions that depart from equilibrium, but it seemed to be more likely related to difficulties in the measurement, because the predicted values from both the new database and the TTNi6 Ni-database are similar.

Fig. 4.16- Calculated partition coefficients of Fe and Nb as a function of solid fraction in the Ni-xFe-3Nb (wt. %) by equilibrium calculations using the new database and the TTNI6 Ni-database (Average experimental method)

Fig. 4.17- Calculated partition coefficients of Fe and Nb as a function of solid fraction in the Ni-xFe-5Nb (wt. %) by Scheil calculations using the new database and the TTNI6 Ni-database (Scheil fitting experimental method)

5. FORMULATION OF A FRECKLING CRITERION FOR Ni-BASED SUPERALLOY VACUUM ARC REMELT INGOTS

This chapter presents the conceptual frame used for the formulation of a criterion for freckling prediction that includes the effect of tilted solidification front. The criterion is based on the maximum local Rayleigh number in the mush layer, and was developed by using Flemings' criterion and assuming the interdendritic liquid flow is governed by the Darcy law. The proposed form preserves the anisotropic nature of the permeability tensor throughout the derivation.

5.1 Formulation of the Local Rayleigh Number Proposed for Freckling Prediction

Consider the solidification of an ingot during VAR remelting process, where the mushy layer has a concave shape and constitutes the two phase transition zone between the molten liquid metal on top of the already solidified region. An ideally paraboloidal shape for the liquidus isotherm surface has been considered, ignoring the electromagnetic effects on the bulk liquid convection that affect the shape of the liquidus and solidus isotherms.¹¹⁸ Therefore, the mush layer and its permeability could be assumed to be locally homogeneous and transversely isotropic due to the four-fold dendritic symmetry, and was deemed that the three-dimensional dendritic array is properly described by a two-dimensional region over a diametral plane of the VAR ingot. Due to the geometry of the mush, the solidification front forms an angle θ with respect to the horizontal plane, that is function of the position along the radius of the ingot as shown in Figure 5.1.

Fig. 5.1- Schematic representation of the mushy layer with tilted solidification front

Here we assume an elementary volume in the mushy layer with the same characteristics as the one defined by M.C. Flemings and G.E. Nereo.³³ This elementary volume is sufficiently large to permit the averaging of the microscopic properties and to have a liquid fraction within, that is exactly equal to the local average, but still it is sufficiently small to be considered as a differential element. The permeability in point O is mathematically described by a second order tensor, which when referred to its principal directions as coordinate system OX_1X_2 , i.e., parallel and perpendicular directions to the

primary dendrites, its non-zero components are the principal values. The permeability tensor can be expressed in its matricial form by equation [5.1] which corresponds to the two-dimensional version of equation [2.20]., that can be defined by experimentally developed functional forms depending on the volume fraction liquid and the arm spacing of primary (λ_1) and secondary dendrites (λ_2) as formulated by Poirier⁵⁰ and are reported on equations [2.22] and [2.23] and are recalled for convenience as equations [5.2] and [5.3].

$$\mathbf{K} = \begin{bmatrix} K_I & 0 \\ 0 & K_{II} \end{bmatrix} \quad [5.1]$$

$$K_I = 3.75 \cdot 10^{-4} \cdot f_L^2 \cdot \lambda_1^2 \quad [5.2]$$

$$K_{II} = 3.62 \cdot 10^3 \cdot f_L^{3.34} \cdot \lambda_1^{0.699} \cdot \lambda_2^{2.73} \quad [5.3]$$

The expressions relating the interdendritic spacing of primary and secondary dendrites with the cooling rate were the ones presented by Auburtin¹¹⁹ and reported in equations [5.4] and [5.5]. The interdendritic spacing units are [m], and the cooling rate ($G \cdot R$) should be given in [Ks^{-1}].

$$\lambda_1 = \frac{150 \cdot 10^{-6}}{(G \cdot R)^{0.33}} \quad [5.4]$$

$$\lambda_2 = \frac{40 \cdot 10^{-6}}{(G \cdot R)^{0.42}} \quad [5.5]$$

The local densities of the solid and liquid phases were considered equal so the flow of interdendritic liquid due to shrinkage was neglected. The only driving force should correspond to the solutal buoyancy, that is proportional to the difference between the density at the liquidus temperature (ρ_0) and the local density at point O (ρ), represented by $\Delta\rho$. Let a potential driving force vector be defined as the gradient density vector multiplied by the length Δz measured from the tip of the dendrites to the point O with magnitude equal to $\Delta\rho$ and acting along the X_1 axis. Under the effect of gravity, the inner product of the potential driving force vector (perpendicular to the isodensity lines) and the gravity acceleration vector g will give the magnitude for the pressure gradient vector as expressed by equation [5.6]. The pressure gradient vector acts in the direction of unit vector n pointing vertically downwards as shown in Figure 5.1.

$$|\vec{\nabla} P| = \Delta\rho \vec{e}_1 \cdot g \vec{n} = \Delta\rho g \cos \theta \quad [5.6]$$

Using the Darcy law,^{120,121} the interdendritic velocity was obtained and presented by equation [5.7] where μ is the dynamic or absolute viscosity of the interdendritic liquid and f_L is the fraction liquid at point O .

$$\vec{v} = \left(\frac{1}{\mu f_L} \right) \cdot \bar{\mathbf{K}} \cdot \vec{\nabla} P = \left(\frac{\Delta\rho g \cos \theta}{\mu f_L} \right) \begin{bmatrix} K_I \cos \theta \\ K_{II} \sin \theta \end{bmatrix} \quad [5.7]$$

It is assumed that the Darcy law of flow through porous media applies in a representative elementary volume in the mushy layer following the methodology proposed by S. Ganesan and D.R. Poirier.³² By using the Flemings criterion, the proposed local Rayleigh number form is obtained by calculating the ratio between the interdendritic velocity vector magnitude and the growth rate as follows:

$$Ra_{-p} = \frac{|\vec{v}|}{R} = \left(\frac{\Delta\rho g \cos \theta}{\mu f_L} \right) \cdot \frac{(K_I^2 \cos^2 \theta + K_{II}^2 \sin^2 \theta)^{\frac{1}{2}}}{R} \quad [5.8]$$

Where R is the growth rate, and K_I and K_{II} are the permeability components in the parallel and perpendicular directions to the primary dendrites respectively, as were defined above. The local Rayleigh number form is obtained by a similar methodology used by Yang¹⁴, with major differences being that in this work the gradient of the pressure is derived differently, the effect of the tilted solidification front is included without the need to know *a priori* the direction of the velocity vector and most importantly, the two dimensional anisotropic characteristic of the permeability tensor is preserved throughout the formulation. It is proposed that the maximum local Rayleigh number obtained by equation [5.8] could be used to predict if a particular alloy, at given thermal conditions, and geometrical characteristics of the mush layer (tilt of the solidification front), will develop freckles or not. As reviewed by Schneider and Beckermann⁵⁶, the two limiting cases describing the microsegregation, the lever rule and the Scheil equation, do not yield considerable differences regarding the macrosegregation behavior. With that in mind, the simpler equilibrium method was used. In order provide accurate estimations of density gradient, it is required to refine the databases available, as the results of chapter four suggested. Since that effort was out of the scope of this research work, it was decided to rely on the calculated values obtained by JMatPro® software¹²² for the solidification path, *i.e.* $f_L(T)$, and also for the calculations of the composition and the density of the interdendritic liquid as functions of temperature. Initially, the calculations of the components K_I and K_{II} were performed directly using the fraction liquid from the solidification path by JMatPro®. Later it was found that the method of harmonic integration proposed by Yang *et al.*⁸¹ and an integration over the liquid fraction using the temperature version of the equation 4 presented by Beckermann *et al.* in reference [82], delivered a better resolution criterion based in the maximum local Rayleigh number. Also, these harmonic integrations showed that the obtained dependence of the local Rayleigh number with the liquid fraction had greater physical meaning. Correspondingly, this combined methodology of integration was assumed then on.

6. VERIFICATION OF THE PROPOSED FRECKLING CRITERION

6.1 Experiments of Directional Solidification at WVU for Criterion Verification

In the proposal of this research work, it was considered the evaluation of the formulated freckle criterion by horizontal directional solidification tests. To validate the prediction capability of the Rayleigh number criterion proposed, own experimental data was pursued by following the plan presented in section 3.2. Unfortunately, the horizontal directional solidification tests did not offered satisfactory results. During the exploration experiments it was found that the sample materials could not be completely melted and homogeneous liquid state for horizontal columnar dendritic growth was not obtained.

Fig. 6.1- Temperature vs Time curves collected for the three zones of DS furnace in trial experiment

The temperatures measured by the control thermocouples located at the different zones of the furnace were recorded and for an example experiment, Fig. 6.2 shows their dependence with time according to the programmed heating and cooling trajectories. Very good response from the controlling unit combined with the necessary slow rates permitted that the real temperatures were very close to the set points expected for almost all times. Noise in form of random peaks was found on the signal registered from thermocouple sensing the temperature at the zone 1. No explanation has been found yet for that erratic variation, but from the random character it showed, most probably its origin is related to electrical influences of the equipment itself or from the pumps and surrounding equipment in the area. Nevertheless, after any faulty data was collected at a time step, in the next collecting step, the value of temperature was refreshed to the realistic baseline. Rates of 90 C/hour were selected to avoid failure of the high purity alumina retort tube, and equalization isothermal stages were included at 800 C during heating and cooling ramps. The total experimental time usually was close to 38 hours and

the starting time was determined appropriately so supervision could be performed during the isothermal holding at the peak temperature.

Water volume rate through the cooling circuit was regularly set at $1.20 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$, and the absolute pressure on the high purity Argon inlet line to 2 psi. The controlled atmosphere was obtained by slow Argon flow of $1 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$ by maintaining the mechanical vacuum pump running during the complete experiment with the outlet needle valve slightly open ($\sim 1/16$ turn open). Although the peak temperatures in this example experiment were 1573 C, 1545 C, and 1400 C for zone 3, zone 2 and zone 1 respectively, the temperature inside the retort tube was certainly below the liquidus point temperature of the sample material which was calculated equal to 1364 C (for this case: heat HV1282 in table 3.3). During the isothermal hold at peak temperature, the axial thermocouple registered an approximately constant temperature of 1469 C, at about 25 mm over the top surface of the sample material. Since the peak temperature of the zone 3 was approximately 30 C below 1600 C, which is the maximum operating temperature recommended by the manufacturer of the furnace (100 C below the type B thermocouples maximum operation temperature) it was decided to suspend the experiments and search for alternative ways of testing the freckling criterion.

6.2 Evaluation of the Criterion for Freckling Prediction Using Experimental Data in the Literature

The evaluation of the proposed criterion for freckling prediction proceeded by using experimental data published by two different research groups involving directional solidification of both commercial and model Ni-based superalloys. Although the criterion formulated was mainly intended to contribute in the accurate prediction of freckling for VAR ingots, the experimental data available in the literature is very limited, so the set of alloys for the evaluation also included alloys designed for powder metallurgy and single crystal superalloys. The experimental parameters (or controlled variables) for the experiments reviewed included the tilt angle of the solidification front, the temperature gradient at the mush–bulk liquid interface, and on the growth rate of the solid crystals. Aiming to preserve simplicity and emphasize the differences of performance attributed to the geometric component of the formulation, the dynamic viscosity of the interdendritic liquid was considered constant with the same value for all alloys and temperatures. The generalized value adopted here was $\mu = 0.004$ in $[\text{Kg m}^{-1} \text{ s}^{-1}]$. The effect of variable viscosity on the proposed local Rayleigh number has been considered for future work.

The complete set of twelve different compositions corresponding to the evaluated alloys is presented in appendix F (table F.1). Due to space limitations, Table 6.1 shows a subset of the total alloys reviewed, where emphasis of presentation in this section was given to the alloys related to alloy 718 and VAR ingots. The complete set of values for the experimental independent variables and the resulting freckle or no-freckle conditions are presented in table F.2 in appendix F. Table 6.2 shows only a subset of table F.2 to exemplify the available data format. It can be noticed that the composition reported for alloy R4007 corresponds to the nominal composition of Alloy IN 718. Also, two variations of IN718 were included with low and high Silicon content, identified by

IN718LSi and IN718HiSi respectively. It is suggested to refer to the original publications for further details about the corresponding experimental procedures.^{14,78,86,119}

Table 6.1. Alloy compositions for the directional solidification experiments used (Subset).

	RN902	RN903	RN5010	R4007	718	718 LSi	718 HSi	Waspaloy
Ni	54.43	70.57	73.93	Bal.	53.94	54.03	53.41	56.89
Co	-	-	-	-	-	0.001	-	13.9
Cr	19.95	20.09	19.98	18.0	18.48	18.0	18.58	19.95
Al	-	-	-	0.5	0.37	0.5	0.38	1.64
Ti	-	-	-	1.0	1.08	1.0	0.90	3.03
Hf	-	-	-	-	-	-	-	-
Mo	-	-	-	3.0	3.07	3.0	2.86	4.59
Ta	-	-	-	-	-	-	-	-
Nb	7.13	8.57	6.36	5.0	4.66	5.0	4.05	-
W	-	-	-	-	-	-	-	-
C	0.014	0.004	0.005	-	-	0.008	0.62	-
B	-	-	-	-	-	-	-	-
Mn	-	-	-	-	-	-	-	-
Si	0.03	0.01	0.01	-	0.23	0.007	-	-
Zr	-	-	-	-	-	-	-	-
Fe	17.75	0.69	0.06	18.0	18.63	18.45	19.45	-
S			0.002	-	-		-	-

Table 6.2-Data from directional experiments reviewed (Subset)

	G (K/mm)	R (mm/min)	Tilt angle α	Freckle
RN902	6.12	1.72	50	N
	4.09	1.5	50	Y
	3.19	1.2	50	Y
	2.92	0.8	50	Y
RN903	4.8	1.36	52	N
	4.39	1.3	52	N
	2.97	1.17	52	N
	2.51	1.0	52	Y
	2.28	0.82	52	Y
	2.53	0.6	52	Y
RN5010	2.14	2.25	82	N
	3.5	0.34	34	Y
R4007	2.19	2.96	33	N
	1.40	2.70	33	Y
	1.02	2.25	33	Y
	0.95	1.59	33	Y

The local Rayleigh number proposed was calculated for the complete set of experimental observations and the resulting maximum values for each experiment were used to construct the graph on Fig. 6.1. In general, the maximum Rayleigh number occurred within the mush layer in the range between 0.5 and 0.7 solid fractions, in fair agreement with the result mentioned previously in section 2.4.2, obtained by Auburtin et al.⁷⁰ Fig. 6.3 presents a frequency diagram for the location of the maximum Rayleigh number expressed by the corresponding liquid fraction. Detailed results per alloy are included in appendix G.

Fig. 6.2- Maximum Rayleigh number vs complete set of experimental data

Fig.6.3 –Frequency graph for maximum Rayleigh number location in the Mush defined by the fraction liquid.

6.2.1 Prediction Resolution

It can be observed from Fig. 6.2 that virtually for all of the alloys it was possible to clearly identify a maximum Rayleigh number value which gave a clear cut between the freckle and no freckle conditions. (In this section ‘Rayleigh number’ will be used to refer to the maximum local Rayleigh number, unless stated otherwise). No overlapping between the freckled and no freckle observed regions was found, but for only one alloy which was MAR-M247. This improved resolution on the freckling prediction, only failed for the particular experiment of MAR-M247 alloy, where a freckling data was found below the approximate threshold value. It is noteworthy that this overlapping observation, corresponding to the fifth experiment for the MAR-M247 subset in table F.2 in the appendix F, had the highest growth rate of the alloy values (2.76 mm/min) and correspondingly its Rayleigh number was the lowest for the group. Freckling did occur although the thermal conditions were not favorable; reflecting the importance of the tilt angle on the freckling potential, which in this experiment was set to 35 degrees.

On Fig. 6.2 an inset image of the low part of the graph with Rayleigh number between 0 and 0.5 is presented for all the alloys. Because the x-axis was ‘compressed’, not all the labels are included in the inset, but the vertical lines can be used to identify the corresponding alloy data. Also, some observations on the region with Rayleigh number greater than 0.5 are left outside the inset. It is evident that if the observations for Waspaloy (labeled as W) and the overlapping point mentioned above of MAR-M247 alloy (labeled as M) are ignored, a line could be drawn at Rayleigh number value of 0.2 which will define a critical value for all the alloys, and defines a limit below which no freckles are found. This value is very close to the critical number of 0.25 proposed by Beckermann and co-workers on reference [82] and supports the tacit hypothesis that the convective instability occurs when the driving force is one forth the impedance magnitude, which should require further research for clarification and complete understanding of the phenomenon.

Some variability characteristics of the threshold for the Rayleigh number should be expected, and can be related with uncertainties and model assumptions used through the derivation. The condition of equilibrium between the interdendritic liquid and the solid dendrites, i.e., the assumption of complete mixing of the interdendritic liquid and infinite diffusion in the solid, the theoretical calculation of liquid density, the assumption of constant viscosity and especially, the empirical nature of the permeability components formulation affect the predictions. Moreover, the experimental determination of the thermal parameters and the potential error on controlling the experiments induce sources of error which finally affect the accuracy of the predictions.

6.2.2 Tilted Solidification Front Effect on the Local Rayleigh Number and Nucleation Sites

The tilt angle effect was to increase the proposed local Rayleigh number over the whole mushy zone, essentially due to a reduction on the resistance to flow. The increase of the Rayleigh number could be linked to a greater combined contribution of the transversal and parallel components of the permeability tensor, making new pathways available for the segregated liquid under the gravitational effect. This explanation is also supported with the observed displacement of the maximum Rayleigh number towards higher locations in the mush, making it easier to start an instable flow with a lower driving force. The proposed form for the local Rayleigh number sheds some light regarding the nucleation sites for freckling. Fig. 6.4 isolates the tilt angle effect by comparing the proposed local Rayleigh number over the mush layer for two experiments performed with alloy IN718LSi (low Silicon) under the same thermal conditions but with different tilt. It is worth noting that the slight increase of tilt by 15 degrees induced instability and the threshold for freckling was surpassed. If there is a region inside a VAR ingot's mush layer with approximately constant cooling rate along an isothermal surface, the thermal conditions could prevent freckling, but if the tilt angle grows, freckles might still evolve. The capacity to resolve the freckling tendency between to points with equal thermal conditions but with different tilt angle, as in Fig. 6.4 could not be possible if the permeability is considered an scalar or isotropic tensor with an averaged value that is a function of solid fraction and the primary dendrite arm spacing like when the Blake-Kozeny expression is used.

Fig. 6.4- Effect of the tilt angle over observations with the same thermal conditions

By using Poirier's formulas, a simple 3-D plot was used to visualize the behavior of the parallel and perpendicular components under the variation of cooling rate and liquid fraction, and correlate these components with the influence of the solidification front tilt angle over the freckling potential. Fig. 6.5 shows the surfaces representing the permeability components as functions of the independent variables cooling rate (K/s) and liquid fraction. For the lowest cooling rates, like the ones observed in the central region of large ingots, the perpendicular component of permeability is greater than the parallel component for almost all the mush layer. This predominance can, from the point of view of the permeability components contribution, explain the industrially known fact that a nonsymmetrical arc in the VAR process will lead to higher freckling potential. The induced tilted solidification front in the ingot's center line will decrease the flow resistance in combination to the freckling favoring local thermal conditions.

Fig.6.5- Poirier's permeability components dependence with cooling rate (K/s) and liquid fraction

6.3 Experimental Design Simulations for Further Verification

As reviewed in section 2.8, near-horizontal directional solidification experiments devoted to produce freckles under controlled conditions on Ni-base superalloys have been seldom reported in the literature. Simpler experimental setups are desired and worth implementing because they will make a needed contribution to expand the set of data available, but most importantly, because constitute a valuable tool to provide additional insight regarding the mechanism of freckle formation, in particular, about the downward flow case.

Experiments of controlled solidification along a direction that forms an acute angle with the gravity vector will also provide more test points to evaluate the predictive accuracy of the freckling criterion formulated in this research. With these benefits in mind, cooperative efforts with researchers from the Processing Development Division at the National Energy Technology Laboratory (NETL-Albany OR) were started directed to develop a new series of near-horizontal directional solidification experiments of Ni-based superalloys to induce freckles in a controlled manner and test the predictions of the proposed criterion.

6.3.1 Antecedent Results at NETL-Albany and Experimental Design Simulations

Previous experiments developed at NETL involved the casting of superalloy 718 into graphite crucibles of 4 in. diameter, contained within green sand molds. As expected,

metallographic analysis revealed the typical solidification macrostructure of a chilled layer of equiaxial grains located at the surface, followed in the radial direction by columnar dendritic grains which extended for about 1 in, and form an angle of approximately 75 deg. with the gravity acceleration vector. Solidification continued at the centerline region with equiaxial grains growth, where a piping void was formed due to solidification shrinkage. Fig. 6.6 shows a picture of the macrostructure present in the upper half region of a semi-diametral plane section. The 4 in. ingot axis is on the right side of the picture. No dendritic columnar grains are observed on the top, because those were sectioned and taken with a slice from the top of the ingot for chemical analysis. The quadrant in the picture has an approximate square shape with 2 in. side and all corners were rounded during metallographic preparation.

Fig. 6.6- Top quadrant extracted from a diametral cut of alloy 718 ingot (4 in. diameter)

It was formulated the question if by controlling the thermal influencing parameters of a similar casting, would it be possible to induce freckles formation at the observed columnar dendrites region.

Metallurgists can control the cooling rates during solidification of castings by numerous ways. These methods include increasing the superheat temperature, increase the weight of the melt by placing more than one piece in the same mold, arranging the location of gateways and risers, changing the thermal properties of materials like the type of sand used in the mold, the type and the thickness of crucibles, etc. From the available data related to the previous experiments, it was known that the casting corresponding to Fig. 6.6 was poured at a temperature with 50 C superheat, the weight of the melt was 6.64 Kg

and the thermo-physical properties of the alloy, the graphite crucible and the mold sand were also known.

To determine the transient heat transfer conditions during solidification and make accurate predictions about the effects of changing the controlling parameters, it is required to determine the heat transfer coefficient in the interface casting-crucible. Because during the first seconds of solidification, the molten metal rapidly transfers heat to the crucible, the solidifying shell contracts, while the crucible or mold expand and a gap is formed in the interface that greatly affects the evolution of the heat flow.^{123, 124}

Modeling of the heat transfer through the interface gap lacks of accuracy, basically because the conduction coefficients of gases are not determined with enough reliability and the gap distance continuously changes during the solidification, hence the methodology usually followed is to experimentally determine the heat transfer coefficient by the inverse method. This methodology consists on performing instrumented experiments of solidification with almost one-directional heat flow (*e.g.* radial heat diffusion during solidification of a sphere), and collecting the temperature profiles in the casting and in the mold material with a high sampling rate. By matching the solution of the one dimensional transient heat transfer equation with the experimental results, the coefficient on the interface can be calculated as a function of temperature.¹²⁵

A variation of the inverse method was used in this research effort to determine the interface heat transfer coefficients in the cylindrical external surface and in the bottom flat surface. Basically, it consisted on using a numerical solution for the simplified two-dimensional domain (given the symmetry of the cylindrical ingot) and comparing the cooling rate obtained on the numerical solution at a selected point at a given time, with the cooling rate indirectly measured on the same location in the ingot by optical microscopy. This is accomplished by use of the empirically developed equation [5.5] which gives a relation between the secondary dendritic arms spacing λ_2 with the cooling rate at the moment when the solidification occurs, which here was taken as the moment when the liquidus isotherm crosses the selected location. The secondary dendrite arm spacing was determined using the conventional metallographic techniques.⁷

By consecutive simulations-iterations, the value of the interfacial heat transfer was calculated and its magnitude was found to be within the ranges published in the textbooks.^{123, 126} To further refine the model and including the differences between the heat transfer in the cylindrical surface with respect to the coefficient in the bottom interface, the numerically calculated temperature gradient vector was used to tune the ratio between the side and bottom coefficients until the numerically obtained temperature gradient vector and the columnar dendrites on the microstructure matched orientation at the interest point at the time when the local solidification occurred (Always keeping the match of the cooling rate at the point). The main difference between the interfacial heat transfer in the side cylindrical metal surface and the crucible, with respect to the heat transfer coefficient in the bottom interface, is that the bottom interface has a closed gap, because the shrinkage pull is compensated by the weight of the solidifying metal and therefore the interfacial characteristics are closer to a case of contact heat transfer than to the conditions of transfer through a shrinkage gap.

The following table 6.3 summarizes the results for the cooling rate and the time it takes to the point of interest to solidify determined by the calibrated numerical simulations and the effects of changing the pre-heat temperature of the crucible and the superheat of the melt. The properties used for alloy 718, graphite crucible and the green sand, where the ones embedded in Comsol software ®.

Table 6.3-Cooling rates and time for liquidus crossing dependence on superheat and initial temperature of the crucible (4 in. diameter ingot)

Ingot diameter: 4 in.		Initial crucible temperature		Measured (from SDAS)
		30 [C]	350 [C]	
Superheat [C]	50	20.26 [C/min] (270 s)	19 [C/min] (280 s)	23 [C/min]
	200	21.00 [C/min] (400 s)	-	
	300	16.06 [C/min] (450 s)	-	
h side		106.25 [Wm ⁻² K ⁻¹]		
h bottom		625 [Wm ⁻² K ⁻¹]		
emissivity top surface		0.2		

The main conclusion from the ‘*virtual*’ experimentation by changing parameters like the superheat and the initial temperature of the crucible is that the heat transfer from the molten metal to the crucible and mold is mainly controlled by the interfacial coefficients. The cooling rate is regulated by the interface and there is no mayor difference to have the crucible preheated over the cooling rate and the time to solidify at the location evaluated. The pre-heating is important fundamentally due to the protection it provides to thermal shock failure of the crucible. Similarly, no substantial gain is obtained by increasing the superheat (impractical value of 300 C was included as an exercise), since the heat flow occurs at almost the same rates, but with the difference that more total heat needs to be extracted and hence the time it takes for solidification at the location of interest is augmented. Table 6.4 shows similar results, but this time the effect of the weight of the melt is included. A rather impractical value of preheat of the crucible is also included for comparison.

Table 6.3- Cooling rates and time for liquidus crossing dependence on superheat and initial temperature of the crucible (8 in. diameter crucible)

Ingot diameter: 8 in.		Initial crucible temperature		Measured (from SDAS)
		350 [C]	425 [C]	
Superheat [C]	50	13.86 [C/min] (380 s)	13.56 [C/min] (390 s)	23 [C/min]
	200	-	11.45 [C/min] (570 s)	
h side		106.25 [Wm ⁻² K ⁻¹]		
h bottom		625 [Wm ⁻² K ⁻¹]		
emissivity top surface		0.2		

Increasing the size of the ingot lowered the cooling rates and extended the time for the point evaluated to solidify.

By using JMatPro ® software, the thermo-physical phase properties for all alloy compositions in table 3.3 were calculated. The cooling rate and the gradient at the solidification front at the representative point in the columnar dendritic structure were numerically determined using the calibrated Comsol model. The conditions for the ‘virtual’ experiment are presented in table 6.4:

Table 6.4-Model input and values obtained for freckle prediction

Parameters		Cooling Rate [C/min]	Gradient [C/m]
Ingot diameter	8 in.	16.122	1889.822
Superheat	100 C		
Crucible init. Temp.	350 C		
Emissivity top surf.	0.2		
h-side	106.2 [Wm ⁻² K ⁻¹]		
h-bottom	625 [Wm ⁻² K ⁻¹]		

By combining the results obtained from JMatPro and the thermal conditions from the numerical solution, the local Rayleigh number proposed for the set of alloys was calculated and presented in Fig. 6.7.

Fig. 6.7- Local Rayleigh number proposed vs liquid fraction for simulated experiments

The maximum values for the local Rayleigh number proposed when evaluating the model alloys available, are one order of magnitude lower than the critical value determined in section 6.2.1. The freckling tendency of model alloys HV1281 and HV1282 are very similar since the variation in Cr amount should not affect greatly the density inversion. It should be recalled that the two compositions were selected aiming to clarify an unexpected result on directional solidification experiments performed on an antecedent

research work by WVU researchers⁹⁷ as explained in section 3.2.1. It is concluded from the simulated experiments, that for any of the alloys in table 3.3, the free cooling of a melt poured at a temperature 100 C higher than its liquidus (superheat of 100), into a 8 in. crucible preheated to 350 C, that is contained in a sand mold, will not deliver the slow cooling conditions required for freckling production. It is required to continue proposing suitable experimental arrangements that may be used to produce freckles on laboratory scale and further evaluate the freckling criterion formulated.

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7. CONCLUSIONS AND FUTURE WORK

In this research work it was aimed to make a contribution toward the final objective of preventing macrosegregation defects in the VAR large ingots of Ni-based superalloys used for electrical power generation applications. Through investigation of the partition coefficients of the major alloying solute elements, integrated with an appropriate review of the theoretical modeling of the phenomena from the perspective of the continuum mechanics, a criterion for the prediction of freckles in Ni-based superalloys was formulated. Experimental data sets available in the literature were used to evaluate the predictions of the criterion and promising results have been obtained. Published results in specialized conferences and journal papers provide guidelines for the composition and processing control required for minimization of macrosegregation occurrence. Successful interactions throughout this research work with partner Universities, Industry and NETL have consolidated a platform for future cooperative research.

In particular, contributions on specific subjects include:

- An experimental methodology was developed to measure the partition coefficients of solute elements during the solidification of Ni-Base superalloys. Its reliability was verified with results published in the literature for the widely studied alloy 718 with satisfying results. Better agreement was found when the measured partition coefficients were compared to predictions performed with newly developed thermodynamical databases, suggesting that improvements in the accuracy in the theoretical predictions can still be obtained and are necessary for accurate freckling prediction.
- A freckling criterion based on the maximum local Rayleigh number was proposed for the re-melting of Ni-based superalloys. Validation with experimental data available showed that the proposed criterion offers improved resolution to discern the observed freckle - no freckled conditions. The critical Rayleigh number deduced was very close to 0.2, which is in accordance with a previously proposed value for superalloys derived by a completely different approach and different set of experimental data. This result contributes in pointing out the need of further understanding of the phenomenon, since an 'ideal' critical value should be equal to one.
- The maximum Rayleigh number obtained with the form proposed usually occurred within a range of liquid fractions that support the hypothesis that the freckles in VAR ingots nucleate and propagate within the mush layer. The effect of a tilted solidification front was addressed and it was corroborated that under the same thermal conditions of solidification, a tilted solidification front induces a higher freckling potential. Most importantly, it showed that the tilt angle influences the potential nucleation sites for freckles in the mush layer.

Future research is needed to clarify the mechanism of freckle formation in superalloy VAR ingots. From the point of view of predicting their formation, new efforts are needed through theoretical and experimental approaches to improve the formulated criterion and further validate its performance. Theoretical approach is essential to address the

difference between the obtained critical Rayleigh number and the expected value of one, and to devise means for extending its applicability to different macroscopic patterns like center segregation. Experimental approach is necessary to propose new designs of arrangements that are simpler and reliable to increase the availability and number of experimental data describing freckles produced in Ni-base superalloys under controlled laboratory conditions. More available data will contribute to support newly proposed nucleation and growth sequences on the mechanism of freckles in VAR ingots and also will provide much needed data points for validation of the criteria proposed.

Actions have already been taken toward the development of the future work during the next years by continued collaboration between researchers in WVU and NETL-Albany teams.

APPENDIX –A

A.1 Solute redistribution equation

The equation of solute mass conservation in the elementary volume is given by:

$$\frac{\partial(\bar{\rho}\bar{C})}{\partial t} = -\nabla \cdot \rho_L g_L C_L \bar{v} \quad [\text{A.1}]$$

Where $\bar{\rho}$ is the local averaged density ($\bar{\rho} = \rho_S g_S + \rho_L g_L$), $\bar{C}$ is the local averaged composition ($\bar{C} = C_S g_S + C_L g_L$), with g_S and g_L representing the solid volume fraction and liquid volume fraction respectively. C_L is the liquid phase composition, ρ_S and ρ_L represent the solid and liquid phase densities respectively, and vector $\bar{v}$ is the local averaged velocity of the liquid relative to the fixed dendritic array (local volume averaged velocity). The conservation of total mass in the elementary volume is given by equation [A.2].

$$\frac{\partial \bar{\rho}}{\partial t} = -\nabla \cdot \rho_L g_L \bar{v} \quad [\text{A.2}]$$

By appropriately grouping and expanding the right hand side (RHS) of equation [A.1] and after substitution in equation [A.2]:

$$\frac{\partial(\bar{\rho}\bar{C})}{\partial t} = C_L \frac{\partial \bar{\rho}}{\partial t} - \rho_L g_L \bar{v} \cdot \nabla C_L \quad [\text{A.3}]$$

The change in solute mass of the volume element per unit time is:

$$\frac{\partial(\bar{\rho}\bar{C})}{\partial t} = \frac{\partial}{\partial t} (\bar{C}_S \rho_S g_S + C_L \rho_L g_L) \quad [\text{A.4}]$$

Where $\bar{C}_S$ is the local average composition of the solid. If it is assumed that the partition coefficient applies at the liquid–solid interface, there is no diffusion to the solid, the density of the solid is constant for all times:

$$\frac{\partial}{\partial t} (\bar{C}_S \rho_S g_S) = k C_L \rho_S \frac{\partial g_S}{\partial t} \quad [\text{A.5}]$$

$$g_S + g_L = 1 \quad [\text{A.6}]$$

Substitution of equations [A.6] and [A.5] into [A.4]:

$$\frac{\partial(\bar{\rho}\bar{C})}{\partial t} = -k C_L \rho_S \frac{\partial g_L}{\partial t} + \rho_L g_L \frac{\partial C_L}{\partial t} + C_L \frac{\partial}{\partial t} (\rho_L g_L) \quad [\text{A.7}]$$

The change in total mass of the volume element per unit time is:

$$\frac{\partial(\rho)}{\partial t} = \frac{\partial}{\partial t}(\rho_s g_s + \rho_L g_L) \quad [\text{A.8}]$$

If the solidification shrinkage is defined by [A.9], then the expression [A.10] is obtained by substituting [A.6], [A.7], [A.8], [A.9] into [A.3]:

$$\beta = (\rho_s - \rho_L) / \rho_s \quad [\text{A.9}]$$

$$\frac{\partial C_L}{\partial t} = -\left(\frac{1-k}{1-\beta}\right) \frac{C_L}{g_L} \frac{\partial g_L}{\partial t} - \bar{v} \cdot \nabla C_L \quad [\text{A.10}]$$

With expressions for the speed of the isotherms and iso-concentrates given by:

$$\frac{dl}{dt} \cdot \nabla T = -\varepsilon \quad [\text{A.11}]$$

$$\frac{dl}{dt} \cdot \nabla C_L = -\frac{\partial C_L}{\partial t} \quad [\text{A.12}]$$

The local solute redistribution equation is obtained:

$$\frac{\partial g_L}{\partial C_L} = -\left(\frac{1-\beta}{1-k}\right) \left(1 + \frac{\bar{v} \cdot \nabla T}{\varepsilon}\right) \frac{g_L}{C_L} \quad [\text{A.13}]$$

APPENDIX –B

B.1 Volume Averaging Method

B.1.1 Fundamental definitions and establishment of theorems and identities

The volume fraction of the liquid phase (g_L) is defined as the fraction of dV occupied by the liquid phase and can be expressed by equation [B.1]:

$$g_L(\bar{x}, t) = \frac{dV_L}{dV}(\bar{x}, t) = (1/dV) \int_{dV} \gamma dv \quad [B.1]$$

Where $dV_L(\bar{x}, t)$ is the part of dV occupied by the liquid phase. The finer scale elementary element dv on equation [B.1] is the microscopic unit element for integration over the averaging volume dV (dv represents the microscopic ξ coordinate). Function $\gamma(\bar{x}, t)$ is called liquid volume distribution function which takes the values 0 or 1, depending if the point under consideration lies on the solid or liquid phase respectively. An analogous expression could be derived for the areal liquid fraction S_L by equation [B.2].

$$S_L(\bar{x}, t) = \frac{dA_L}{dA}(\bar{x}, t) = (1/dA) \int_{dA} \gamma(\bar{r}, t) da \quad [B.2]$$

Any microscopic quantity ψ with a field distribution within the microscopic averaging volume dV has a macroscopic representative average Ψ associated to the centroidal point C. The microscopic quantity of the liquid phase ψ_L in the averaging volume (e.g. density, temperature, velocity) will have a macroscopic representing quantity given by equation [B.3]:

$$\Psi_L(\bar{x}, t) = (1/dV) \int_{dV} \psi_L(\bar{r}, t) \gamma(\bar{r}, t) dv \quad [B.3]$$

The intrinsic volume average of quantity ψ_L is defined by equation [B.4]:

$$\Psi_L^L(\bar{x}, t) = \frac{\Psi_L(\bar{x}, t)}{g_L} = (1/dV_L) \int_{dV} \psi_L(\bar{r}, t) \gamma(\bar{r}, t) dv \quad [B.4]$$

For example, the liquid phase mass density (ρ_L) is related to the intrinsic volume averaged mass density by equation [B.5] as follows:

$$\rho_L^L(\bar{x}, t) = (1/dV_L) \int_{dV} \rho_L(\bar{r}, t) \gamma(\bar{r}, t) dv \quad [B.5]$$

In the construction of the macroscopic conservation equations sometimes is necessary to express the mass average of a certain microscopic quantity in dV . The mass averaged macroscopic variable is given by equation [B.6].

$$\bar{\Psi}_L(\bar{x}, t) = (1/\rho_L^L g_L dV) \int_{dV} \rho_L(\bar{r}, t) \psi_L(\bar{r}, t) \gamma(\bar{r}, t) dv \quad [B.6]$$

Within the averaging volume, the local temperature and the liquid composition are considered uniform, and coupled by the liquidus curve, so the equation [B.7] is valid and when this condition is met, the intrinsic average of any quantity ψ_L will be equal to its mass averaged value and equation [B.8] can be written.

$$\rho_L^L(\bar{x}, t) = (1/dV_L) \rho_L \int_{dV} \gamma(\bar{r}, t) dv = \rho_L \quad [B.7]$$

$$\bar{\Psi}_L(\bar{x}, t) = \Psi_L^L(\bar{x}, t) = \frac{\Psi_L(\bar{x}, t)}{g_L} \quad [B.8]$$

Similar expressions could be obtained for any of the solid phase quantities ψ_s . In order to obtain the averaged conservation equations for the macroscopic representation of the mushy zone, it is required to apply basic theorems and identities on which the technique relies. Theorem I (also referred as first theorem), gives a relation between the average of the spatial derivative to the spatial derivative of the average, and is presented in equation [B.9]:

Theorem I

$$\left(\frac{1}{dV}\right) \int_{dV} (\nabla \psi_L) \gamma(\bar{x}, t) dv = \nabla \left[\left(\frac{1}{dV}\right) \int_{dV} \psi_L \gamma dv \right] + \left(\frac{1}{dV}\right) \int_{a^*} \psi_L \bar{n}_{ls} da^* \quad [B.9]$$

Where a^* is the interfacial area between the liquid and the solid phase inside dV and the unit vector $\bar{n}_{ls}$ is the outward normal of the microscopic element of area da^* pointing from the liquid to the solid phase.

Theorem II (also referred as second theorem), relates the average of a time derivative to the time derivative of the averaged quantity by equation [B.10]:

Theorem II

$$\left(\frac{1}{dV}\right) \int_{dV} \left(\frac{\partial \psi_L}{\partial t}\right) \gamma(\bar{x}, t) dv = \frac{\partial}{\partial t} \left[\left(\frac{1}{dV}\right) \int_{dV} \psi_L \gamma dv \right] - \left(\frac{1}{dV}\right) \int_{a^*} \psi_L \bar{w} \cdot \bar{n}_{ls} da^* \quad [B.10]$$

Vector w in equation [B.10] represents the velocity of the microscopic liquid-solid interface. There are four identities involving the deviation of a microscopic quantity in point P, with position given by vector r , with respect to its mass averaged quantity associated with C, the centroidal point of dV .

The deviation of a microscopic quantity from its mass averaged value is given by equation [B.11].

$$\varphi_L(\vec{r},t) = \psi_L(\vec{r},t) - \bar{\Psi}_L(\vec{x},t) \quad [\text{B.11}]$$

Given that $\bar{\Psi}_L(\vec{x},t)$ is constant for the averaging volume, the mass average of the deviation of ψ_L is zero. This is expressed by the first identity in equation [B.12]:

Identity (i)

$$\bar{\tilde{\psi}}_L(\vec{r},t) = 0 \quad [\text{B.12}]$$

The second identity is given by equation [B.13], where the long bar over the product of two variables means that the mass averaging is taken after the product.

Identity (ii)

$$\overline{\tilde{\psi}_L \bar{\Phi}} = 0 \quad [\text{B.13}]$$

Where $\bar{\Phi}$ represents the mass average of any other microscopic quantity ϕ_L and is given by equation [B.6]. The third identity is stated by equation [B.14] and it includes the mass averaged value of the product of the deviations of microscopic quantities ψ_L and ϕ_L , and is denominated ‘dispersion quantity’.

Identity (iii)

$$\overline{\psi_L \phi_L} = \bar{\Psi}_L \bar{\Phi}_L + \overline{\tilde{\psi}_L \tilde{\phi}_L} \quad [\text{B.14}]$$

The fourth identity is given by equation [B.15] as follows:

Identity (iv)

$$\left(\frac{1}{dV}\right) \int_{dV} \rho_L \tilde{\phi}_L \bar{\Psi}_L \gamma dv = 0 \quad [\text{B.15}]$$

B.1.2 Conservation of mass equation

The microscopic conservation equation for the interdendritic liquid is given by:

$$\frac{\partial \rho_L}{\partial t} + \nabla \cdot \rho_L \vec{v}_L = 0 \quad [\text{B.16}]$$

Where vector $\vec{v}_L$ is the microscopic velocity of the interdendritic liquid. By multiplying equation [B.16] by γ and averaging over dV equation [B.17] is obtained.

$$\left(\frac{1}{dV}\right) \int_{dV} \left(\frac{\partial \rho_L}{\partial t}\right) \mathcal{V} dv + \left(\frac{1}{dV}\right) \int_{dV} (\nabla \cdot \rho_L \bar{v}_L) \mathcal{V} dv = 0 \quad [\text{B.17}]$$

By using the first and second theorems and keeping in mind the assumption that the temperature and liquid composition are uniform in the averaging volume, so the microscopic density is uniform in dV , equation [B.17] could be transformed to equation [B.18].

$$\frac{\partial}{\partial t}(\rho_L g_L) + \nabla \cdot (\rho_L g_L \bar{V}_L) + \left(\frac{1}{dV}\right) \int_{a^*} \rho_L (\bar{v}_L - \bar{w}) \cdot \bar{n}_{ls} da^* = 0 \quad [\text{B.18}]$$

Where the $\bar{V}_L$ bar, is the mass averaged velocity of the interdendritic liquid (i.e. the macroscopic velocity of the interdendritic liquid) according to the definition in equation [B.6]. A similar equation can be obtained for the solid phase:

$$\frac{\partial}{\partial t}(\rho_s g_s) + \nabla \cdot (\rho_s g_s \bar{V}_s) + \left(\frac{1}{dV}\right) \int_{a^*} \rho_s (\bar{v}_s - \bar{w}) \cdot \bar{n}_{sl} da^* = 0 \quad [\text{B.19}]$$

Where vector $\bar{v}_s$ is the microscopic velocity of the solid, vector $\bar{V}_s$ bar is the mass averaged velocity of solid, vector $\bar{n}_{sl}$ is the outward normal of the microscopic element of area da^* pointing from the solid to the liquid phase.

The solid density ρ_s is assumed to be equal to the intrinsic averaged solid density, similarly to the case for liquid phase expressed in equation [B.7]. The liquid mass loss due to solidification equals the mass gain by the solid phase, so the integrals on equations [B.18] and [B.19], are equal in magnitude but with opposite sign ($\bar{n}_{sl} = -\bar{n}_{ls}$). By adding these two equations, and recalling the assumption of static solid phase, equation [B.20] is obtained:

$$\frac{\partial}{\partial t}(\rho_s g_s + \rho_L g_L) + \nabla \cdot \rho_L g_L \bar{V}_L = 0 \quad [\text{B.20}]$$

Because ρ_L is uniform within dV , and recalling equation [B.8], equation [B.20] could be written as:

$$\frac{\partial}{\partial t}(\rho_s g_s + \rho_L g_L) + \nabla \cdot \rho_L \bar{V}_L = 0 \quad [\text{B.21}]$$

Equation [B.21] is consistent with equation [A.8] for the conservation of total mass in the mush, although the approach taken by Flemings and Nereo (1967) on the development of the local solute redistribution equation is completely different, and conceptually closer to the diffusive mixture theory reported below on section 2.1.3. If and only if the solid and liquid densities are equal and time independent within dV ($\rho_L = \rho_s = \rho$) and using $g_L + g_s = 1$, equation [B.21] becomes:

$$\nabla \cdot \vec{V}_L = 0 \quad [\text{B.22}]$$

B.1.3 Conservation of momentum equation

Maintaining the assumption of stationary solid, the microscopic momentum conservation equation for the liquid is given by:

$$\frac{\partial}{\partial t}(\rho_L \vec{v}_L) + \nabla \cdot \rho_L \vec{v}_L \vec{v}_L = -\nabla p_L + \rho_L \vec{g} + \nabla \cdot \sigma_L^{(2)} \quad [\text{B.23}]$$

Where vector $\vec{g}$ is the gravity acceleration, p_L is the pressure and $\sigma_L^{(2)}$ is the deviatoric component of the material stress tensor for the liquid element. By multiplying equation [B.23] by the liquid phase distribution equation and taking the average over dV , equation [B.24] is obtained:

$$\left(\frac{1}{dV}\right) \int \frac{\partial}{\partial t}(\rho_L \vec{v}_L) \chi dv + \left(\frac{1}{dV}\right) \int (\nabla \cdot \rho_L \vec{v}_L \vec{v}_L) \chi dv = -\left(\frac{1}{dV}\right) \int \nabla p_L \chi dv + \left(\frac{1}{dV}\right) \int \rho_L \vec{g} \chi dv + \left(\frac{1}{dV}\right) \int \nabla \cdot \sigma_L^{(2)} \chi dv \quad [\text{B.24}]$$

After applying the basic theorems and identities presented previously, and neglecting the exchange of momentum due to the volume change and the so-called ‘average dispersion vector’ as well, the LHS of equation [B.24] can be written as:

$$\left(\frac{1}{dV}\right) \int \frac{\partial}{\partial t}(\rho_L \vec{v}_L) \chi dv + \left(\frac{1}{dV}\right) \int (\nabla \cdot \rho_L \vec{v}_L \vec{v}_L) \chi dv = \frac{\partial}{\partial t}(\rho_L g_L \bar{V}_L) + \nabla \cdot (\rho_L g_L \bar{V}_L \bar{V}_L) \quad [\text{B.25}]$$

The RHS of [B.24] also should receive further treatment involving the basic theorems and identities. With considerations of equilibrium of forces and no slip on the interface, and including the assumptions of Newtonian liquid, constant viscosity in the averaging volume dV , and the validity of the Darcy Law, the conservation of momentum equation becomes:

$$\rho_L \left[\left(\frac{1}{g_L}\right) \frac{\partial \bar{V}_L}{\partial t} + \left(\frac{1}{g_L^2}\right) \bar{V}_L \cdot \nabla \bar{V}_L \right] = -\nabla p_L + \rho_L \vec{g} + \left(\frac{\mu}{g_L}\right) \nabla^2 \bar{V}_L - \mu \left[\left(\frac{1}{K^{(2)}}\right) \cdot \bar{V}_L + \frac{C^{(3)}}{g_L^3} : (\bar{V}_L)(\bar{V}_L) \right] \quad [\text{B.25}]$$

APPENDIX – C

C.1-Composition of the Model Alloys Prepared

Table C.1 Composition of model alloys subsystem Ni-Fe-Nb [Wt. %] (Bal. Ni)

Alloy ID (target)		Nb	Fe
Alloy 7 (Ni-3Nb-5Fe)	Min.	3.46	4.66
	Max.	4.67	5.58
	Aver.	3.88	5.283
Alloy 8 (Ni-5Nb-5Fe)	Min.	3.45	4.66
	Max.	4.67	5.36
	Aver.	4.06	5.01
Alloy 9* (Ni-3.0Nb-10Fe)	Min.	-	-
	Max.	-	-
	Aver.	3.35	10.41
Alloy 10 (Ni-5Nb-10Fe)	Min.	6.01	9.96
	Max.	6.02	9.98
	Aver.	6.0	9.90
Alloy 11 (Ni-3Nb-18Fe)	Min.	1.95	15.93
	Max.	6.83	19.06
	Aver.	3.39	17.98
Alloy 12 (Ni-5Nb-18Fe)	Min.	4.83	18.68
	Max.	4.86	19.01
	Aver.	4.84	18.71
Alloy 13 (Ni-3Nb-36Fe)	Min.	1.57	29.62
	Max.	5.48	38.9
	Aver.	2.7	36.31
Alloy 14 (Ni-5Nb-36Fe)	Min.	5.9	35.60
	Max.	6.3	35.75
	Aver.	6.14	35.70

*Discarded

Table C.2 Composition of model alloys subsystem Ni-Cr-Fe-Nb [Wt. %] (Bal. Ni)

Alloy ID (target)		Nb	Cr	Fe
Alloy 15 (Ni-3Nb-18Cr-10Fe)	Min.	1.57	17.6	9.81
	Max.	3.93	19.47	10.57
	Aver.	3.13	18.68	10.08
Alloy 16 (Ni-3Nb-20Cr-18Fe)	Min.	3.2	18.75	17.69
	Max.	3.8	20.37	18.4
	Aver.	3.5	19.55	17.97
Alloy 17 (Ni-5Nb-18Cr-18Fe)	Min.	5.38	17.66	17.77
	Max.	5.93	17.94	18.04
	Aver.	5.64	17.83	17.87
Alloy 18 (Ni-5Nb-20Cr-10Fe)	Min.	5.41	19.71	9.89
	Max.	5.82	19.83	9.9
	Aver.	5.61	19.77	9.89

Table C.3 Composition of model alloys produced subsystem Ni-Cr-Al [Wt. %] (Bal. Ni)

Alloy ID (target)		Al	Cr
Alloy 19 (Ni-0.6Al-15Cr)	Min.	0.43	14.14
	Max.	0.86	14.6
	Aver.	0.568	14.36
Alloy 20 (Ni-0.6Al-20Cr)	Min.	0.18	18.61
	Max.	0.63	19.96
	Aver.	0.425	19.22
Alloy 21 (Ni-1.0Al-18Cr)	Min.	0.85	14.45
	Max.	1.39	15.02
	Aver.	1.08	14.80
Alloy 22 (Ni-1.5Al-20Cr)	Min.	1.46	19.82
	Max.	1.84	21.24
	Aver.	1.62	20.63

Table C.4 Composition of model alloys subsystem Ni-Cr-Fe-Al [Wt. %] (Bal. Ni)

Alloy ID (target)		Al	Cr	Fe
Alloy 23 (Ni-0.6Al-15Cr-10Fe)	Min.	0.43	14.71	10.22
	Max.	0.46	15.2	10.5
	Aver.	0.45	15	10.34
Alloy 24 (Ni-0.6Al-20Cr-10Fe)	Min.	0.58	21.29	20.5
	Max.	0.9	21.63	21.11
	Aver.	0.7	21.43	20.65
Alloy 25 (Ni-1.0Al-15Cr-20Fe)	Min.	0.73	14.98	20.22
	Max.	1.13	15.34	20.75
	Aver.	0.96	15.14	20.42
Alloy 26 (Ni-0.6Al-20Cr-20Fe)	Min.	0.55	21.19	20.5
	Max.	0.9	21.63	21.11
	Aver.	0.70	21.43	20.65

Table C.5 Composition of model alloys subsystem Ni-Cr-Ti [Wt. %] (Bal. Ni)

Alloy ID (target)		Ti	Cr
Alloy 27 (Ni-0.5Ti-15Cr)	Minimum	0.72	14.62
	Maximum	0.95	14.98
	Average	0.81	14.74
Alloy 28 (Ni-1.5Ti-15Cr)	Minimum	1.64	14.99
	Maximum	1.81	15.76
	Average	1.71	15.38
Alloy 29 (Ni-0.5Ti-20Cr)	Minimum	0.5	20.46
	Maximum	0.48	20.42
	Average	0.58	21.0
Alloy 30* (Ni-1.5Ti-20Cr)	Minimum	-	-
	Maximum		
	Average		

*Discarded

APPENDIX – D

D.1-Fitting EDS data to Scheil equation Code

The MatLab© function code used to fit the experimental EDS data to the Scheil equation for microsegregation is included below. The function calculates the error function defined in equation 5 and returns the partition coefficient that minimizes it, i.e., the best fit partition coefficient. The input information required are the ordered vector of original EDS measurements, 'Cs' (according to segregation tendency), the original content of the alloying element in the parent melt 'Co', the assumed minimum apparent solid fraction 'fsmin' (to make up for the low probability of hitting the real dendrite core), and the maximum reached apparent solid fraction before quenching 'fsmax'. An arbitrary data set is included for exemplification purposes.

```
%% Code to determine Partition Coefficients from fitting to Scheil Equation
% Created by Jairo A. Valdes Ortiz.
% Department of Mechanical and Aerospace Engineering, West Virginia University
% Morgantown, West Virginia, Fall 2007
%
% Function Syntax
% partcoeff(Cs,Co,fmin,fmax)
% Cs is a vector containing the EDS data
% Co is the Melt Composition (Parent alloy)
% fsmin is the Apparent Solid Fraction at the Estimated Core Dendrite
% fsmax is Maximum Reached Apparent Solid Fraction Determined by Metallographic
Analysis
function partcoeff(Cs,Co,fmin,fmax)
% Example Data
% % Original Data Collected by EDS
% Cs = [0.95, 1, 1, 1.03, 1.05, 1.06, 1.07, 1.19, 1.2, 1.25, 1.25, 1.25, 1.26, 1.31, 1.37,
1.44, 1.5, 1.64];
% % Initial value of Parent Composition [wt%]
% Co = 2.06;
% % Apparent Solid Fraction at the Estimated Core Dendrite
% fsmin = 0.05;
% % Maximum Reached Apparent Solid Fraction Determined by Metallographic
Analysis
% fsmax = 0.9;

% Number of Data Points Entered
ndata = length(Cs);
% Estimated Values of the Apparent Solid Fraction
fs = linspace(fsmin,fsmax,ndata);

% Plotting original data of Apparent Solid Fraction vs. Solid Composition (Measured)
figure(1); grid on; hold on; title('Original data for Apparent Solid Fraction vs. Solid
Composition (Measured)');
```

```
xlabel('Apparent Solid Fraction'); ylabel('Solid Composition (Measured) [wt%]');
plot(fs,Cs,'ro');
```

```
% Possible values for the Partition Coefficient
```

```
k = (0:0.001:1.5);
```

```
n = length(k);
```

```
% Error function to determine the Partition Coefficient
```

```
%  $y_k = (C_s - k \cdot C_o \cdot (1 - f_s)^{(k-1)})^2$ 
```

```
yk(1:n) = 0;
```

```
for j=1:n
```

```
    yk(j) = 0;
```

```
    for i=1:length(fs)
```

```
        yk(j) = yk(j) + (Cs(i) - k(j)*Co*(1-fs(i))^(k(j)-1))^2;
```

```
    end
```

```
end
```

```
% Results
```

```
[ykmin,id] = min(yk);
```

```
kmin = k(id);
```

```
disp('Best fit Partition Coefficient');
```

```
disp(kmin)
```

```
figure(2); grid on; hold on;
```

```
xlabel('partition coefficient'); ylabel('fitting error [wt%^2]')
```

```
plot(k,yk,'b'); plot(kmin,ykmin,'rx');
```

APPENDIX – E

E.1-Results for Fitting EDS data to Scheil equation graphs

Fig.E.1-Fitting error to Scheil equation vs. Partition Coefficient of Chromium in alloy Ni-17.17Cr-3Nb

Fig. E.2-Fitting error to Scheil equation vs Partition Coefficient of Niobium in alloy Ni-5Fe-5Nb

Fig. E.3-Fitting error to Scheil equation vs Partition Coefficient of Fe in alloy Ni-5Fe-3Nb

Fig. E.4-Fitting error to Scheil equation vs. Partition Coefficient of Aluminum in alloy Ni-20Cr-4.9 Al-6Nb

Table E.1-Measured partition coefficients by profile fitting

K_{Nb}	K_{Cr}	K_{Al}
0.785	1.02	1.11

The MDTA experiments were performed for all the alloys of the Ni-Cr-Ti subsystem, following the same methodology previously described. On the SEM/EDX examination of the samples, it was observed that the amount of Titanium on the bulk of the samples was highly reduced, while a continuous layer of oxide with high content of Ti was found in all processed samples.

Although the data collected was not suitable to determine the partition coefficient of Ti, its presence influenced the Chromium partition coefficient. The result for target Alloy 28 is showed in Fig. E.5. Modifications for the procedure of MDTA experiments are required in order to prevent the depletion of Titanium observed.

Fig.E.5-Partition Coefficient of Chromium for target Ni-1.5Ti-15Cr

APPENDIX – F

F.1-Compositions of the Alloys for Criterion Verification

Table F.1. Alloy Compositions for the Complete Set of Directional Solidification Experiments Used In the Criterion Validation.

	RN902	RN903	RN5010	R4007	CMSX-11B	RENE 88	Nim 80A	718	718 LSi	718 HSi	Waspaloy	MAR M247
Ni	54.43	70.57	73.93	Bal.	59.02	Bal.	76.0	53.94	54.03	53.41	56.89	57.42
Co	-	-	-	-	5.51	13.0	-	-	0.001	-	13.9	10.35
Cr	19.95	20.09	19.98	18.0	11.34	16.0	19.5	18.48	18.0	18.58	19.95	8.3
Al	-	-	-	0.5	2.93	2.1	1.4	0.37	0.5	0.38	1.64	5.79
Ti	-	-	-	1.0	3.93	3.7	2.4	1.08	1.0	0.90	3.03	0.78
Hf	-	-	-	-	0.16	-	-	-	-	-	-	1.73
Mo	-	-	-	3.0	0.48	4.0	-	3.07	3.0	2.86	4.59	0.62
Ta	-	-	-	-	6.23	-	-	-	-	-	-	4.08
Nb	7.13	8.57	6.36	5.0	0.13	0.7	-	4.66	5.0	4.05	-	-
W	-	-	-	-	9.9	4.0	-	-	-	-	-	10.93
C	0.014	0.004	0.005	-	-	0.03	0.06	-	0.008	0.62	-	-
B	-	-	-	-	-	0.015	0.03	-	-	-	-	-
Mn	-	-	-	-	-	-	0.3	-	-	-	-	-
Si	0.03	0.01	0.01	-	-	-	0.3	0.23	0.007	-	-	-
Zr	-	-	-	-	-	-	0.06	-	-	-	-	-
Fe	17.75	0.69	0.06	18.0	-	-	-	18.63	18.45	19.45	-	-
S			0.002	-	-	-	-	-		-	-	-

F.2-Complete Set of Data Corresponding to the Directional Solidification Experiments Used to Validate the Criterion Proposed.

Table F.2- Data from Directional Experiments Reviewed - Complete

	G (K/mm)	R (mm/min)	Tilt angle α	Freckle
RN902	6.12	1.72	50	N
	4.09	1.5	50	Y
	3.19	1.2	50	Y
	2.92	0.8	50	Y
RN903	4.8	1.36	52	N
	4.39	1.3	52	N
	2.97	1.17	52	N
	2.51	1.0	52	Y
	2.28	0.82	52	Y
	2.53	0.6	52	Y
RN5010	2.14	2.25	82	N
	3.5	0.34	34	Y
R4007	2.19	2.96	33	N
	1.40	2.70	33	Y
	1.02	2.25	33	Y
	0.95	1.59	33	Y
CMSX-11B	2.3	1.0	0	N
	2.3	1.0	0	N
	3.0	1.0	0	N
	0.7	6.0	0	N
	2.3	1.0	20	Y
	0.7	6.0	20	N
	3.0	1.0	20	Y
	0.7	6.0	20	N
	2.3	1.0	35	Y
	0.7	6.0	35	N
	3.0	1.0	35	Y
	0.7	6.0	35	N
René 88	0.9	6.0	35	N
	2.6	1.0	35	Y
	0.9	6.0	20	N
	2.6	1.0	20	Y
	1.1	1.0	0	Y
Nim80A	1.1	6.0	35	N
	2.6	1.0	35	Y
	1.1	6.0	20	N
	2.6	1.0	20	Y
	1.5	1.0	0	Y
718	1.0	6.0	35	N
	2.6	1.0	35	Y

	1.0	6.0	20	N
	2.6	1.0	20	Y
	1.4	1.0	0	Y
718 LSi	1.5	6.0	35	N
	2.9	1.0	35	Y
	1.5	6.0	20	N
	2.9	1.0	20	N
	2.0	1.0	0	N
718 HiSi	0.9	6.0	35	N
	3.5	1.0	35	Y
	0.9	6.0	20	N
	3.5	1.0	20	Y
	3.1	1.0	0	Y
Waspaloy	0.7	1.98	0	N
	2.3	1.92	0	N
	1.4	1.32	18	Y
	1.4	1.20	25	Y
	1.1	3.0	34	N
	1.4	1.32	34	Y
	3.1	1.26	34	Y
MAR-M247	1.3	1.3	0	Y
	1.2	1.86	0	N
	1.3	1.32	18	Y
	1.3	1.32	24	Y
	1.1	2.76	35	Y
	1.3	1.32	35	Y

APPENDIX –G

G.1-Maximum local Ra number criterion proposed. Evaluation for each Alloy

-Critical value of 0.2 could be used, No freckles formed below this point.

(universal, except Waspaloy)) - One overlapping experiment only: MAR-M247 point 5

G.2-Local Rayleigh number proposed vs fraction liquid for all alloys

RN 902					
FRECKLE	DATA	R (mm/min)	G*R (C/min)	G (C/mm)	Tilt
N	1	1.72	10.5264	6.12	50
Y	2	1.5	6.135	4.09	50
Y	3	1.2	3.828	3.19	50
Y	4	0.8	2.336	2.92	50

RN 903

FRECKLE	DATA	R (mm/min)	G*R (C/s)	G*R (C/min)	G (C/mm)	Tilt
N	1	1.36	0.1088	6.528	4.8	52
N	2	1.3	0.09511667	5.707	4.39	52
N	3	1.17	0.057915	3.4749	2.97	52
Y	4	1	0.04183333	2.51	2.51	52
Y	5	0.82	0.03116	1.8696	2.28	52
Y	6	0.6	0.0253	1.518	2.53	52

R5010

FRECKLE	DATA	G*R (C/min)	R (mm/min)	Tilt
N	1	4.82	2.25	82
Y	2	1.18	0.34	24

R4007

FRECKLE	DATA	G*R (C/min)	R (mm/min)	Tilt
N	1	6.47	2.96	33
Y	2	3.8	2.7	33
Y	3	2.29	2.25	33
Y	4	1.51	1.59	33

CMSX11B

FRECKLE	DATA	G (C/cm)	R(mm/min)	G*R (C/min)	Tilt
N	1	23	1.0	2.30E+00	0
N	2	23	1.0	2.30E+00	0
N	3	30	1.0	3.00E+00	0
N	4	7	6.0	4.20E+00	0
Y	5	23	1.0	2.30E+00	20
N	6	7	6.0	4.20E+00	20
Y	7	30	1.0	3.00E+00	20
N	8	7	6.0	4.20E+00	20
Y	9	23	1.0	2.30E+00	35
N	10	7	6.0	4.20E+00	35
Y	11	30	1.0	3.00E+00	35
N	12	7	6.0	4.20E+00	35

Rene88

FRECKLE	DATA	G (C/mm)	R(mm/min)	G*R (C/min)	Tilt
N	1	0.9	6	5.4	35
Y	2	2.6	1	2.6	35
N	3	0.9	6	5.4	20
Y	4	2.6	1	2.6	20
Y	5	1.1	1	1.1	0

Nim80

FRECKLE	DATA	G (C/mm)	R(mm/min)	G*R (C/min)	Tilt
N	1	1.1	6	6.6	35
Y	2	2.6	1	2.6	35
N	3	1.1	6	6.6	20
Y	4	2.6	1	2.6	20
Y	5	1.5	1	1.5	0

IN718

FRECKLE	DATA	G (C/mm)	R (mm/min)	G*R (C/min)	tilt
N	1	1	6	6	35
Y	2	2.6	1	2.6	35
N	3	1	6	6	20
Y	4	2.6	1	2.6	20
Y	5	1.4	1	1.4	0

IN718LSi					
FRECKLE	DATA	G (C/mm)	R (mm/min)	G*R (C/min)	Tilt
N	1	1.5	6	9	35
Y	2	2.9	1	2.9	35
N	3	1.5	6	9	20
N	4	2.9	1	2.9	20
N	5	2	1	2	0

IN718HiSi					
FRECKLE	DATA	G (C/mm)	R (mm/min)	G*R (C/min)	Tilt
N	1	0.9	6	5.4	35
Y	2	3.5	1	3.5	35
N	3	0.9	6	5.4	20
Y	4	3.5	1	3.5	20
Y	5	3.1	1	3.1	0

Waspaloy					
FRECKLE	DATA	R (mm/min)	G (C/mm)	G*R (C/min)	Tilt
No	1	1.98	0.7	1.386	0
No	2	1.92	2.3	4.416	0
Y	3	1.32	1.4	1.848	18
Y	4	1.2	1.4	1.68	25
No	5	3	1.1	3.3	34
Y	6	1.32	1.4	1.848	34
Y	7	1.26	3.1	3.906	34

MAR-M247					
FRECKLE	DATA	R (mm/min)	G (C/mm)	G*R (C/min)	Tilt
Y	1	1.3	1.3	1.69	0
N	2	1.86	1.2	2.232	0
Y	3	1.32	1.3	1.716	18
Y	4	1.32	1.3	1.716	24
Y	5	2.76	1.1	3.036	35
Y	6	1.32	1.3	1.716	35

APPENDIX-H
H.1-Experimental Design Simulation

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