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Sub-Solidus and Super-Solidus Heat Treatments of a Single Crystal Superalloy

by

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A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

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Abstract

Cast Ni-base superalloys are highly heterogeneous due to coring during solidification. To increase high temperature capabilities, modern single crystal (SX) superalloys are heavily alloyed with the refractory elements, W, Ta, and Re. As a consequence, the microsegregation of these alloys is more pronounced leading to higher eutectic fractions and chemical instability. Hence, heat treatment of modern SX alloys is becoming increasingly challenging, time consuming and expensive. This thesis investigates the homogenization-solutionization behaviour of an experimental Ni-base single crystal superalloy over a wide temperature range including sub-solidus and super-solidus temperatures.

The first part of the thesis studies conventional stepwise homogenization-solution heat treatments. After characterizing the specimens by metallography, phase fraction analysis, and electron microprobe analysis (EPMA), a *continuously heating* procedure is proposed for heavily alloyed SX superalloys to reduce homogenization-solution heat treatment time without causing incipient melting. Though the solidus temperature is the upper limit for conventional stepwise homogenization-solution heat treatments, the second part of this research identifies that a controlled super-solidus exposure gives rise to significant microstructural refinement without affecting the SX structure. A modification to Bridgman SX processing involving a *super-solidus* step is proposed in the third part of the thesis. The effect of super-solidus temperature and mould withdrawal rate on the microstructure, microporosity and eutectic fraction of super-solidus processed specimens are presented and compared with conventionally cast single crystal specimens. The potential advantage of this modified method is illustrated by performing solution heat treatments on both super-solidus and normally processed specimens followed by eutectic phase fraction analysis.

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Nomenclature

CC:	conventionally cast
C_0 :	nominal composition
C_{core} :	concentration in the dendrite core
C_{ID} :	concentration in the interdendritic region
DoE:	design of experiment
DS:	directionally solidified
DSC:	differential scanning calorimetry
EDX:	energy dispersive x-ray
EPMA:	electron probe microanalysis
ESR:	electroslag refining
FCC:	face-centered cubic
G:	temperature gradient
G_L :	temperature gradient across the liquidus temperature
γ :	gamma solid solution phase
γ' :	gamma prime precipitate phase
k' :	equilibrium partition ratio
LMC:	liquid metal cooling
MC-NG:	mono cristal nouvelle génération
NIMS:	National Institute of Materials Science
PDAS:	primary dendrite arm spacing
PWA:	Pratt and Whitney Aircraft
SEM:	scanning electron microscope
SX:	single crystal
TCP:	topologically close-packed
TET:	turbine entry temperature
TLP:	transient liquid phase
T_L :	liquidus temperature
T_S :	solidus temperature

ΔT :	solidification temperature range (T_L - T_S)
V:	growth velocity
VIM:	vacuum induction melting
WDX:	wavelength dispersive x-ray
XRD:	x-ray diffraction

1. Introduction

1.1 An Overview of Superalloys

Superalloys are a class of unique metallic alloys which possess superior high temperature mechanical properties over extended periods of time. With high homologous temperature ($T_{\text{operating}} / T_{\text{melting}}$), tensile strength, toughness, and resistance to creep and surface degradation, they can serve in the most arduous conditions of high temperature, high mechanical pressure, thermomechanical fatigue, erosion, hot corrosion and high temperature oxidation. Depending on the major alloying element, there are three types of superalloys: nickel-base alloys, cobalt-base alloys, and iron-base alloys; the Ni-base superalloys being the most popular and widely used. The Ni-base superalloys are sometimes called the daughters of stainless steel as the primary face centered cubic austenitic structure, which can dissolve large quantities of a wide range of alloying additions, was developed from stainless steel [1]. Though started as a simple Fe-Ni-Cr alloy, modern superalloys are perhaps the most compositionally complex alloys with typically a dozen alloying elements.

Though superalloys have varied applications from heat exchangers to space shuttles, they are most commonly used in the hot section components such as combustors, guide vanes, turbine blades and discs of gas turbine engines [2-4]. Figure 1.1 illustrates how historically the introduction of successive commercial gas turbine engines has taken advantage of the improving high temperature capabilities of

superalloys. As the efficiency of a gas turbine engine is directly dependent on the turbine entry temperature (TET), there is an ever existing quest to increase TET which is a challenge, as well as the driving force, to improve the high temperature capabilities of superalloys [3-6].

As implied by Figure 1.1, the design and development of Ni-base superalloys has been an on-going activity since their initial inception. Over the last sixty years there has been extensive research on the science and processing of superalloys. Consequently, there has been a substantial effort to understand the heat transfer characteristics so that efficient internal cooling systems for hot section components can be effectively designed [4, 6]. From the materials engineering and processing side, significant efforts have been made to increase the high temperature capabilities of superalloys by improved alloy design; clean melting technologies such as vacuum arc melting (VAM) and electro slag refining (ESR); casting technologies such as directional solidification (DS) and single crystal growth (SX); and coating technologies such as metallic diffusion bond coatings and ceramic thermal barrier coatings [5, 6].

The current state of technology for high pressure turbine blades is to design single crystal (SX) alloys with compositions that provide superior mechanical and thermal properties and corrosion resistance without compromising the microstructural stability. The ‘design of experiment’ (DoE) approach, which led to the development of generations of SX alloys with a monotonic increase in the additions of refractory

elements, is being replaced slowly by thermodynamic analytical and computational techniques. With the increasing alloying content, the solid solubility limit of Ni is reached or exceeded leading to chemical and microstructural instabilities most often revealed by the formation of deleterious topologically close packed (TCP) phases [5, 6]. Hence understanding the phase stabilities of these alloys has become increasingly important. However, modern SX alloys, being the multicomponent systems of typically 12 alloying elements, it is indeed difficult to understand the role of individual elements within the complex alloy either computationally or through experiments. Figure 1.2 schematically illustrates how constraints of the desired processing and application properties are limiting the design space available for future superalloys [6].

1.2 Background of This Research

The present thesis research is a part of the on-going collaborative research program between Carleton University and the National Research Council, which aims to understand the physical metallurgy of SX Ni-base superalloy system by studying the correlations of chemistry, microstructure, and properties of experimental alloys. As part of this program, a pilot scale Bridgman furnace has been commissioned at the Department of Mechanical and Aerospace Engineering, Carleton University [7]. The directional solidification (DS) process modeling and simulation studies have been completed and optimum processing conditions have been established [8]. A series of experimental superalloys have been designed and cast in single crystal form [9]. The microsegregation studies of as-cast SX alloys have been completed and the roles of

critical alloying additions such as Re and Ru on the microstructures have been understood [10, 11].

1.3 Objective and Scope of This Thesis

This thesis further extends the foregoing research by studying the homogenization and solutionization response of the indigenously designed experimental alloys. This research is required since solidified SX alloys are highly heterogeneous due to microsegregation during solidification. To make them suitable for high temperature applications, SX superalloys undergo an extensive heat treatment cycle involving a homogenization-solution step followed by precipitation aging. With increased amounts of slow diffusing refractory additions in modern SX alloys, post-solidification homogenization-solution heat treatment has become very complex, requiring a long heating solutioning time, and, is therefore, expensive. There is a necessity and a technical challenge to develop efficient homogenization-solution methods for heavily alloyed superalloys. The objective of the present thesis is to study conventional homogenization-solution techniques and to introduce innovative methods of homogenizing and solutionizing heavily alloyed SX alloys to reduce the cycle time and energy consumption.

This thesis consists of literature reviews of SX superalloys and heat treatments of SX alloys in the second and third chapters respectively. Chapter 4 provides the details of material selection and experimental methods. Chapter 5 discusses the microstructural response to a conventional homogenization-solution approach and provides

guidelines for designing homogenization-solution heat treatments for newly formulated superalloys. Chapter 6 introduces a new and innovative ‘super-solidus’ approach to homogenization that involves exposing SX alloys to temperatures above the incipient melting temperature. Chapter 7 extends this new ‘super-solidus’ approach to demonstrate its incorporation into the Bridgman SX method. Finally, Chapter 8 summarizes the major findings of this research work and suggests potential areas of study for future work.

2. Single Crystal Superalloys

2.1 Introduction

Ni-base superalloys are classified into wrought alloys and cast alloys. The wrought alloys are generally polycrystalline in nature and are used for making rolled or forged gas turbine components such as combustor cans or turbine discs respectively. The cast alloys, which are further classified into conventionally cast, directionally solidified and single crystal alloys, are generally used for making components such as turbine blades and guide vanes with intricate aerodynamic shapes and internal cooling channels. These complex components are universally produced by the investment casting method.

Figure 2.1 illustrates the grain structure of conventionally cast, directionally solidified and single crystal turbine blades [12]. The components produced by conventional investment casting have randomly oriented equiaxed grains as there is no unique directionality to the solidification of the liquid alloy in the shell mould. Such polycrystalline cast components are referred to as conventionally cast (CC) parts. It is possible to impose some directionality in the solidification pattern of the casting. A special type of furnace with directional cooling, the Bridgman furnace, is used to produce directionally solidified (DS) castings with columnar grains and, hence, reducing the grain boundary area. Finally, a special grain selection modification to the shell mould assembly coupled with the directional cooling during solidification can

eliminate grain boundaries completely to produce single crystal (SX) castings in which the entire component is made of only one grain.

2.2 Significance of Grain Boundary Elimination

Gas turbine blades operate in the most arduous environment of high temperature, high pressure, particulate erosion and high temperature corrosion [4-12]. Being rotating parts there is an added complication of centrifugal force exerting axial tension on the blades during the turbine operation. Despite an appropriate cross sectional area, designed to ensure a tensile stress level well below the elastic limit of the material, time dependent inelastic deformation, or creep, operates constantly in these components during turbine operation. While creep deformation is a slow process at lower temperatures ($T_{\text{operating}} / T_{\text{melting}} < 0.25$), it becomes significant at higher temperatures. Over a period of time, creep strain accumulates in the axial direction causing the elongation of the blades reducing the clearance between the blade tip and the stationary shroud of the turbine. The prevention of blade tip-shroud contact limits the service life of blades and therefore maximum creep resistance becomes an important high temperature material property for the turbine blades [4-6, 12].

Figure 2.2 compares the creep performance of the superalloy MAR-M200 in conventionally cast, directionally solidified and single crystal forms showing the superior creep property of the single crystal structure [13]. Grain boundary diffusion (Coble creep), lattice diffusion (Nabarro-Herring creep) and dislocation creep are the operating creep mechanisms at different temperature and stress levels [14]. To use the

material over a wide range of temperatures and stresses, it is important to strengthen a superalloy against all these operating creep mechanisms. Solid solution strengthening and precipitation hardening methods are employed to reduce lattice diffusion and dislocation creep. The grain boundary diffusion is reduced by increasing the average grain size and thereby decreasing grain boundary area. Hence, for the same set of operating conditions, a turbine blade with the larger grains has a lower creep strain rate than a blade of the same material with finer grains. Further, the elimination of transverse grain boundaries delays the onset of tertiary creep as evident from the creep curves in Figure 2.2. This explains why directionally solidified turbine blades with large columnar grains have better creep properties than their polycrystalline counterparts.

Single crystal structures exhibit even better creep behaviour as the grain boundary diffusion (Coble creep) is almost completely eliminated. Possibly more importantly, the complete elimination of grain boundaries in single crystal alloys provides a special technical advantage during the alloy design. Creep fracture is almost always intergranular despite strengthening by precipitating carbides and borides along grain boundaries in CC and DS alloys. There is no necessity of grain boundary strengtheners in the single crystal alloys and, hence, additions of carbon and boron are avoided. These alloying additions being melting point depressants, their absence elevates the solidus and liquidus temperatures of the superalloys. Hence, significant redesign of alloy compositions with increased solvus and incipient melting temperatures is made possible for SX alloys [15, 16]. For the same operating

temperature, a lower homologous temperature ($T_{\text{operating}} / T_{\text{melting}}$) is imposed in SX alloys compared to CC or DS alloys. This contributes to a reduced creep rate, thereby increasing the service life of turbine blades. Conversely, for a comparable creep rate to CC and DS alloys, a higher operating temperature can be realized in SX alloys.

2.3 Microstructural Features of SX Superalloys

Figures 2.3 and 2.4 illustrate the evolution of high temperature capability and the evolution of microstructure respectively for Ni-base superalloys. For the highest temperature capability the polycrystalline microstructure has been slowly replaced by columnar and finally single crystal microstructures. Over a period of time, there has been a significant variation in the type and distribution of secondary phases, both desired and undesired shown at the top and bottom of Figure 2.4 respectively. However, the matrix or the continuous primary phase, which is an austenitic solid solution of Ni, remained the same. Modern single crystal superalloys are designed to have only two phases: the matrix phase gamma (γ) and the intermetallic Ni₃Al,Ti precipitate gamma prime (γ') phase and together these two phases form the duplex γ/γ' microstructure shown in Figures 2.5 and 2.6. However, undesired embrittling topologically close packed phases (TCPs) such as Sigma (σ), Mu (μ), and Laves do appear as a result of the high temperature operation due to chemical instabilities in the alloys [17]. These phases are rich in some of the solute elements and cause matrix depletion of important alloying additions and deteriorate the properties of the alloys. For chemical stability and optimal creep properties, a careful balance of the alloying additions is required and ensuring microstructural stability poses a great challenge

during alloy design. In modern alloys, a high volume fraction of about 70% γ' is designed for the optimal creep strength, Figure 2.7. The γ - γ' interface plays a major role in the creep resistance, a higher volume fraction of γ' decreases the stability of this interface [18].

2.4 Crystallographic Features of γ and γ'

The crystal structures of the γ and γ' phases are shown schematically in the Figure 2.8. The solid solution γ phase which forms the continuous matrix has the disordered face centered cubic crystal structure (FCC) in which some of the solvent atoms (Ni) are substituted by solute atoms. The secondary precipitate phase γ' has an ordered $L1_2$ superlattice structure with the face centered position occupied by Ni atoms and the cubic corner positions occupied by either Al or Ti atoms. The ordered cubic phase γ' and the disordered cubic phase γ have similar lattice parameters and they have cubic-cubic crystallographic orientation relationship denoted as:

$$\begin{aligned} \{100\}_{\gamma} // \{100\}_{\gamma'} \\ \langle 010 \rangle_{\gamma} // \langle 010 \rangle_{\gamma'} \end{aligned}$$

As shown in the Figure 2.9, γ' exists as coherent precipitates in the form of cuboids with γ - γ' interfaces normal to $\langle 001 \rangle$ directions. The electron diffraction pattern of a SX-superalloys (Figure 2.10) shows γ' superlattice reflections such as $\{100\}$, $\{210\}$ superimposed on regular FCC reflections (from both γ and γ') such as $\{200\}$, $\{110\}$ indicating crystallographic coherency of these phases. The small difference in the

lattice parameter between γ and γ' forms a misfit strain (δ) at the interfaces which is expressed as:

$$\delta = 2 \left[\frac{a_{\gamma'} - a_{\gamma}}{a_{\gamma'} + a_{\gamma}} \right]$$

Depending on the alloy composition, the misfit can be either positive or negative. This is an important parameter as it affects interfacial energy and thereby influences the creep behaviour of the alloy and the morphology of γ' precipitates [18-19].

2.5 Development of SX Superalloys

Typically about a dozen alloying elements are added to SX superalloys. These alloying additions in general partition between γ and γ' phases; some partition more strongly than others. A summary of the effects of individual elements is given in Table 2.1. Figure 2.11 illustrates the variation of individual alloying additions in superalloys over 50 years. Table 2.2 gives a summary of compositions of different generations of commercial single crystal superalloys. In general, elements such as Cr, Co, Mo, W and Re act as solid solution strengtheners as they partition more strongly to the matrix γ phase. Elements such as Al, Ti and Ta partition strongly to γ' phase, and hence they act as precipitate formers or precipitate strengtheners. Of these elements, Cr and Al are oxide formers and help in surface protection as well. Ru helps in retarding TCP phase formation hence acts as a microstructure stabilizer [19].

Single crystal casting technology, which was introduced by Pratt & Whitney in 1980, was considered a revolutionary processing advance. This led to the development of

first generation SX superalloys with significantly superior high temperature properties than conventionally cast and directionally solidified alloys. Increasing additions of slow diffusing refractory elements such as Mo, W, Ta and, in particular, Re proved to effectively enhance the creep properties. This led to the development of second generation SX superalloys, which are characterized by the addition of 3 wt% Re. Further demand to increase the creep resistance of the superalloys was met by increased additions of refractory elements leading to the development of third generation SX alloys, which are characterized by the addition of 6 wt% Re [19].

While creep resistance is very important, it is equally important to maintain microstructural and chemical stability. The third generation alloys suffered a major set-back in this regard [20-21]. Increased Re additions helped in improving the creep properties, but decreased the microstructural stability of the system due to precipitation of deleterious topologically close packed (TCP) phases. Though reductions in Cr content helps in reducing the propensity of TCP phase formation, this dramatically decreases the hot corrosion resistance of the alloy. The development of overlay coating technology on superalloys provides improved hot corrosion resistance [21-22].

The other problem of increased additions of refractory elements is the increased heterogeneity of as-cast microstructure which made the homogenization of these alloys a long process and as a result expensive. The drawbacks of third generation alloys are partly overcome in the fourth generation alloys especially by the addition

of Ru along with Re. The addition of Ru reduces the microsegregation during the dendritic solidification and improves resistance to creep and TCP phase formation [21-23]. The first fourth generation superalloy, MC-NG was developed as a collaborative effort by Onera, Snecma and Turbomeca in France [23]. Subsequently, EPM-102, another fourth generation alloy, was jointly developed by NASA, General Electric and Pratt and Whitney in United States [24]. The National Institute of Materials Science (NIMS) of Japan has been actively involved in designing a number of SX alloys referred to with TMS prefix. NIMS is now in the process of developing next generation alloys with the increased additions of refractory elements such as Nb, Ta, Mo and Re for strengthening along with increased Ru content for phase stability. It has been claimed that alloy TMS-162 with high Ru and Mo displays the best temperature capability of any superalloy [25]. This appears to be an alloy that marks the beginning of the transition from fourth to fifth generation SX superalloys.

2.6 Directional Solidification (DS)

For directional solidification, a special furnace with directional cooling capability called a Bridgman furnace is used. A schematic of an industrial Bridgman furnace is shown in Figure 2.12. A Bridgman furnace has three sections: a melting chamber, a furnace chamber and a mould withdrawal chamber. To avoid oxidation of the melt, the furnace operates under vacuum so that the furnace chamber acts as a radiation furnace. As illustrated in Figure 2.13, the mould withdrawal chamber is separated from the furnace chamber by a horizontal insulating baffle which acts as the adiabatic section. As shown in Figure 2.14 the mould is placed on a water-cooled copper chill

platen situated in the mould withdrawal chamber whose vertical motion is controlled using a stepper motor or hydraulic system. During directional solidification, the mould is raised into the hot furnace chamber through a central hole in the insulating baffle. The melted alloy is then poured into the mould while the furnace chamber is maintained above the melting temperature of the alloy. The copper chill plate cools the bottom of shell and polycrystalline solidification starts at the bottom. The mould assembly is then withdrawn from the hot chamber through the adiabatic zone into the cold chamber at a prescribed speed by lowering the copper chill platen as illustrated in Figure 2.14. During withdrawal, grain growth takes place in the opposite direction of the heat flux. Eventually, polycrystalline grains grow vertically into columnar grains as illustrated schematically in Figure 2.15, as competitive growth allows the most favorably oriented grains to overgrow less favourably oriented remaining grains. Hence, only a few columnar grains remain in the casting. In the case of cubic crystals such as Ni-base alloys, $\langle 001 \rangle$ is the preferred crystallographic growth direction. Hence, directionally solidified superalloy castings have $[001]$ oriented columnar grains along the axis of the casting. Formation of strong $[001]$ texture in the DS superalloy structures is shown with the help of pole figures in Figure 2.16. However, the remaining crystallographic directions such as $[010]$, $[100]$ of these columnar grains are not matched. Hence, longitudinal grain boundaries formed between them.

2.7 Single Crystal Growth

Single crystals are also cast by directional cooling in a Bridgman furnace. However, to produce a single crystal casting, an important modification to the DS process is necessary. The Bridgman method of producing SX castings is depicted in Figure 2.17. A spiral pig-tail shaped cavity at the bottom of the shell extends off the mould cavity and acts as the grain selector during the solidification stage. When the liquid alloy is poured into the shell mould, it fills the spiral cavity as well. When the mould is slowly withdrawn from the hot chamber into the cold chamber, regular directional solidification takes place at the starter block, Figure 2.17. As the solidification proceeds through the spiral cavity, columnar grains are restricted in the spirals one by one. Finally, only one grain which is most favorably oriented will be successful in growing beyond the pig-tail cavity. Figure 2.18 illustrates how the single crystal grain selection takes place in the pig-tail geometry. The emerging grain acts as the single crystal seed. Hence the rest of the casting will have single crystal structure [26].

The pig-tail grain selection method is a reasonably reliable method of growing single crystals as the spiral geometry in the mould cavity selects only one grain as the seed crystal and hence ensures single crystal structure to the casting. However, it should be noted that the grain selector can not control the secondary axes ($[010]$, $[100]$) orientation of the selected grain. For some applications of the SX alloys, even the secondary axes orientation is important. In such situations, the pig-tail grain selector method is replaced with the seed crystal method [27]. In this method, a properly oriented single grain crystal is placed at the bottom of the shell as shown in Figure

2.19. The casting grown coherently on this seed crystal will be a single crystal with both the primary and secondary crystallographic axes controlled. The seed crystal method is a simple modification. However, the seed used should be defect free. If there are extra grains in the seed crystal, then the casting produced will be directionally solidified with the columnar grains instead of single crystal. Therefore the seed crystal should be examined thoroughly and its single crystal structure confirmed before using. However, the important advantage of this method is that both the primary and secondary crystallographic orientation of the casting can be controlled by properly orienting the seed crystal in the shell mould.

2.8 Heat Transfer during Directional Solidification

The Bridgman method appears as a simple directional cooling arrangement for producing DS and SX castings. However, to ensure defect free castings, very carefully controlled heat transfer is necessary. A simple heat transfer model based on reference [28] is provided. A more detailed model has been discussed elsewhere [8].

Consider a casting being withdrawn at a constant speed, v from a Bridgman hot chamber maintained at the temperature T_1 , into a cold chamber maintained at the ambient temperature T_0 . The hot chamber acts as a heat source and the cold chamber acts as a heat sink as shown schematically in Figure 2.20.

The rate of heat extraction from the casting is given by Newton's law of cooling, and is expressed as:

$$q = h_{eff}(T_1 - T_0) \quad (2.1)$$

Where, h_{eff} is the effective heat transfer coefficient of the mould surface emerging in the cold chamber as withdrawal proceeds. If a steady state axial heat flow through the casting is considered, and a planar solid-liquid interface at a sharp melting point, T_m is assumed such that $T_l > T_m > T_0$, the following condition exists at the solid-liquid interface with temperature $T = T_m$:

$$k_s \left(\frac{\partial T}{\partial x} \right)_s - k_l \left(\frac{\partial T}{\partial x} \right)_l - Lv = 0 \quad (2.2)$$

where k_s and k_l are thermal conductivities of solid and liquid and L is the volumetric latent heat of fusion. The axial temperature fields in liquid and solid portions of the casting are given by the following equations:

$$T(x)_{liquid} = T_l - (T_l - T_m) \exp(-\beta_{liquid} x) \quad (2.3)$$

$$T(x)_{solid} = T_0 + (T_m - T_0) \exp(-\beta_{solid} x) \quad (2.4)$$

$$\beta_{liquid} = \frac{vc}{k_l} \quad (2.5)$$

$$\beta_{solid} = \left\{ \left(\frac{2h_{eff}}{k_s r} \right) + \left(\frac{vc}{2k_s} \right)^2 \right\}^{1/2} - \left(\frac{vc}{k_s} \right) \quad (2.6)$$

where c is the volumetric heat capacity of the alloy.

For a simple casting geometry of a cylindrical rod of radius r , the maximum withdrawal speed for steady state heat transfer is given by the following relationship:

$$v = \frac{1}{c} \left(\frac{2h_{eff}k_s}{r} \right)^{1/2} \left(z^{1/2} - z^{-1/2} \right) \quad (2.7)$$

$$z = \frac{L + c(T_1 - T_0)}{L + c(T_1 - T_m)} \quad (2.8)$$

Hence, the maximum withdrawal speed of mould can be calculated. At a higher withdrawal speed, solidification will not be complete before liquid enters the cold chamber with remaining liquid solidifying due to radiation from the hot mould surface to the surrounding cold zone. This affects the single crystal structure by forming defects such as freckles and stray grains. Hence, mould withdrawal speed is an important parameter in the Bridgman process. It is important to note from equation 2.7 that the withdrawal speed is inversely proportional to the square root of the casting radius. Hence, withdrawal becomes very slow for castings with large cross sectional areas.

Axial conduction through the casting is the only significant heat transfer mode at the beginning of the mould withdrawal. As the mould withdrawal proceeds, the vertical surface of the mould is exposed to the cold chamber. Hence, radiation heat transfer between mould surface and the water cooled cold chamber becomes significant. The

effective heat transfer coefficient becomes a combination of conduction and radiation heat transfer coefficients (h_c , h_r) expressed as:

$$h_{eff} = h_c + h_r \quad (2.9)$$

$$h_c = \frac{k_s}{x} \quad (2.10)$$

$$h_r = \frac{\sigma(\varepsilon T^4 - \alpha T_0^4)}{T - T_0} \quad (2.11)$$

where x is the height of the solid casting, σ is the Stephen-Boltzman constant, ε is the emissivity of the mould surface and α is the absorptivity of the cold chamber walls. For more accurate analysis, the conduction heat transfer coefficient for shell mould (h_{shell}), radiation heat transfer coefficient between the casting surface and inner mould surface (h_{gap}) are also included.

2.9 Dendritic Solidification

Superalloys are multicomponent systems with typically a dozen alloying elements. The nominal compositions of these alloys are changing with alloy development often with the introduction of new alloying additions. Hence, it is very difficult to trace the solidification sequence of these alloys on a phase diagram. However, based on the duplex microstructure with known volume fractions of γ and γ' phases, a SX superalloy can be superimposed on the binary phase diagram of Ni-Al. Hence, an idea

of the solidification sequence of a superalloy can be obtained as shown the Figure 2.21. The liquid alloy has one homogeneous composition represented by the central vertical line. However, the first fraction to solidify forms γ and the last fraction to solidify forms γ - γ' eutectic with the compositions shown as vertical lines dropped from the horizontal tie lines drawn from the liquidus and solidus points of the alloy. As a result, the solidified alloy will have a range of compositions instead of an average homogeneous composition. As an ideal case scenario, if a planar front solidification with no solid diffusion and no liquid mixing is assumed, the non equilibrium solidification sequence as illustrated in Figure 2.22 could be expected. The initial transient stage followed by steady state region ensures solidification of the single phase γ . However, solute enrichment in the liquid during the final transient stage leads to a eutectic reaction. Hence, irrespective of the alloy composition and solid growth rate, the as-solidified microstructure will have a fraction of γ solid solution and a fraction of γ - γ' eutectic [29].

The alloy undergoes constitutional undercooling caused by inevitable perturbations in the initial planar solid front. This instability in the solid-liquid interface leads to cellular type solidification against the direction of heat flux [29, 30]. This leads to the formation of γ - γ' eutectic between the cored γ cells as depicted in Figures 2.23. The cells grow in the opposite direction to the heat flow which is perpendicular to the solid-liquid interface. The cellular structure changes its morphology with changes in temperature gradient and growth kinetics as illustrated in Figure 2.24. The intercellular perturbations caused by increased growth rate and imposed temperature

gradient leads to a dendritic structure with dendrite arms grown in preferred crystallographic direction. Because of anisotropic properties such as solid-liquid interface energy and growth kinetics, the dendrites grow along the preferred crystallographic direction. For cubic materials such as Ni-base superalloys, the primary and higher order dendrite arms form along $\langle 001 \rangle$ directions [29-31].

3. Homogenization and Solutionization of SX Superalloys

3.1 The Solidified Microstructure

As stated in the previous section, the solidified microstructure of a superalloy is dendritic with primary and higher order dendrite arms oriented along $\langle 001 \rangle$, which is the preferred crystallographic growth direction for cubic crystals. Because of this, it is straight forward to recognize a single crystal superalloy by observing the solidified transverse microstructure. Figure 3.1 compares the solidified structure of a single crystal with a directionally solidified structure [31]. The transverse section of Figure 3.1(a) reveals properly aligned dendrites with no grain boundaries. All the primary dendrite arms or dendrite cores are aligned along the $\langle 001 \rangle$ direction and the secondary arms are oriented perpendicularly along four $[010]$ type directions. Hence there is a common crystallographic relationship between two adjacent dendrite arms, thereby forming a single grain across the solidified section. Figure 3.1(b) shows how the single crystal structure breaks down when there is a misalignment of dendrites, forming two grains separated by a high angle grain boundary. If two adjacent dendrites growing with a slight crystallographic mismatch impinge on each other a so-called low angle grain boundary results and, even if low grain boundaries ($<10^\circ$) occur, then the resulting structure is usually still classified as single crystal [31-32]. As the orientation mismatch is minimal between two adjacent subgrains, it is difficult to recognize a low angle grain boundary in a low resolution optical micrograph.

As single crystals do not have high angle grain boundaries, the effect of low angle boundaries on the mechanical properties is being studied [33]. Single crystal superalloys usually contain microscopic discontinuities or micropores due to the shrinkage of isolated interdendritic liquid during the final stage of solidification [34]. An unetched transverse section, shown in Figure 3.2, reveals the presence of micropores at the interdendritic region of a solidified crystal. As these pores act as stress raisers and sources of crack initiation, it is desirable to have lower microporosity levels for improved fatigue and creep behaviour [34-36].

3.2 Microsegregation

Figure 3.3 illustrates a typical transverse section of a cast single crystal superalloy after chemical etching. The contrasting dark and grey regions clearly indicate that the solidified structure is chemically segregated. During solidification through the mushy zone, some of the solute elements prefer to remain in the liquid phase while some elements preferentially diffuse to the solid phase forming a chemical heterogeneity in the solidified structure. During the dendritic solidification, cores of dendrite arms form first and the interdendritic liquid solidifies at a later stage [37]. It has been established that in superalloys, heavier and high melting point solutes preferentially diffuse to the dendrite cores, while lighter elements such as Al and Ti segregate to the interdendritic liquid. Since Al and Ti are the γ' forming elements, as the solidification progresses, the residual interdendritic liquid in the mushy zone is enriched with these elements and finally undergoes the following eutectic reaction:

Consequently, the solidified microstructures of Ni-base superalloys are highly heterogeneous with a significant fraction of γ - γ' eutectic phase in the interdendritic region [38, 39]. This naturally occurring phenomenon as illustrated on the phase diagram of Figure 2.21 is called coring or microsegregation.

Figure 3.4 shows the chemical composition maps of a transverse section obtained from electron probe microanalysis (EPMA) confirming the microsegregation in solidified alloy. Also, chemical composition profiles obtained by EPMA line scans, shown in Figure 3.5, indicate the extent of microsegregation between the dendrite core and the interdendritic eutectic. It is clear that Co, Cr, W, Mo, and Re segregate preferentially to the dendrite cores, while Ti, Al, and Ta segregate preferentially to the interdendritic region. From the EPMA profiles, it should be noted that these solutes do not completely diffuse to either the dendrite core or interdendritic regions. However, they partition between core and the interdendritic region (ID). Hence, the microsegregation is quantified as a partition ratio of the concentration of an element in the dendrite core (the first fraction to solidify) to the concentration in the interdendritic region (the last fraction to solidify) expressed as:

$$k' = \frac{C_{core}}{C_{ID}} \quad 3.2$$

where k' is the partition ratio. Elements Mo, W, and Re have k' greater than 1 since they segregate to the dendrite cores. In contrast, the elements Al, Ti, and Ta, have k' less than 1 as they segregate to interdendritic region. Ru has k' value close to one as it

does not show any preferential segregation, but more importantly, the addition of Ru reduces the partition ratio of all elements [39].

There are two important effects of microsegregation in the solidified structure: chemical heterogeneity and microstructural heterogeneity. These effects have a direct impact on the mechanical properties and hence the performance of superalloys as high temperature materials. Since the γ - γ' interface plays a major role in the development of strength and creep resistance, it is always desirable to have a fine and uniform precipitates throughout the microstructure. Figure 3.6 clearly illustrates the variations in the size and morphology of γ' precipitates in solidified superalloy. This is not a desirable microstructure as the γ' precipitates in the interdendritic region are coarse, irregular shaped and have lost the coherent cuboidal shape with controlled misfit at the interface – it is the controlled and low misfit from which the good mechanical properties arise.

The chemical heterogeneity in the solidified structure leads to chemical instabilities. Dendrite cores in the solidified structure being rich in Cr and Re are preferred locations for formation of the embrittling TCP phases that degrade both the creep and fatigue resistance of the alloy [40]. Consequently, SX alloys in the solidified state can not be used for the intended high temperature application. To promote chemical homogeneity and eliminate coring, as well as achieve microstructural uniformity, solidified alloys undergo a homogenization-solution heat treatment. To obtain the

desired uniform γ/γ' duplex microstructure, the homogenization-solution heat treatment is followed by γ' precipitation aging [41].

To increase the high temperature capabilities, modern single crystal (SX) superalloys contain higher quantities of the refractory elements W, Ta, and Re. As a consequence, the microsegregation of these alloys is more pronounced leading to higher eutectic fractions and greater chemical instability [38-41]. Consequently, the time and energy to homogenize-solutionize these alloys is increased from first to third generation SX superalloys. For example, the standard homogenization-solution heat treatment of the third generation SX superalloy, CMSX-10, takes as long as 45 hours as compared to 3 hours required for its first generation counter part (CMSX-2), and 16 hours for its second generation counter part (CMSX-4). Hence, homogenization-solutionization of modern SX alloys is becoming an increasingly challenging, time consuming and expensive process [41]. For the most part, the specific heat treatment processes of commercial as-cast superalloys are treated as empirical proprietary knowledge by superalloy designers and producers.

3.3 Homogenization-Solution Heat Treatment

Ni-base superalloys are subjected to precipitation hardening or age-hardening in which γ' is the hardening precipitate phase and γ is the primary matrix phase. The precipitate hardening heat treatment has two important steps: solutionizing and aging. The solutionization heat treatment also serves as a chemical homogenization treatment to counter the partitioning of elements between the dendrite cores and

interdendritic regions. In addition, the solution treatment should dissolve the γ' phase (both within the dendrites and interdendritic eutectic) into the γ matrix by either isothermal or stepwise heat treatment, between the γ' solvus and solidus temperatures, which is often referred to as the 'solutioning window'[41, 42]. The alloy is then cooled quickly to a low room temperature. The aging treatment involves holding the alloy at sub-solvus temperatures to obtain fine and uniform γ' precipitates within the γ matrix. To promote a bimodal distribution of γ' phase, aging often involves high temperature primary aging, followed by lower temperature secondary aging steps [41, 42].

3.4 Challenges

Despite the existing understanding, it is challenging to design homogenization-solution heat treatments for superalloys because of the following reasons.

1) Differential Scanning Calorimetry (DSC) is generally employed to obtain phase transformation temperatures. However, it is difficult to identify the solvus and solidus temperatures of solidified superalloy from the DSC profiles because of the interference of these transformations due to chemical heterogeneity that causes broadening of the corresponding endothermic and exothermic peaks [43, 44].

2) It may be possible to resolve solidus and solvus peaks in a DSC thermograph following some degree of homogenization. However, these phase transformation

temperatures not only vary with the heating or cooling rate but also with the degree of homogenization [41, 44].

3) It is not uncommon that segregation of trace elements P, S, Si, B and Hf promote incipient melting in the interdendritic region at very low temperatures [45-47]. A highly segregated solidified microstructure may have a local solidus temperature in the interdendritic region significantly lower than the average solvus temperature within the dendrites. Under such a circumstance, a super-solvus homogenization-solution heat treatment leads to localized melting at the interdendritic region and complete solutionizing becomes almost impossible.

4) Figure 3.7 shows the typical morphology of the eutectic phase in the interdendritic region. As can be seen from the figure, the eutectic structure appears as discrete pools at the interdendritic region and can consist of several coarse γ' blocks separated by narrow channels of γ , which is the continuous matrix phase. The complete dissolution of eutectic γ' is difficult because of its coarse blocky morphology with a low surface area per unit volume ratio which makes it dissolve very slowly into the γ matrix [48].

Of all the stated difficulties, perhaps the most challenging problem in designing the homogenization-solution heat treatment is undesirable incipient melting due to a low local solidus temperature. During the dendritic solidification, because of microsegregation, the last fraction of the liquid solidifies within the interdendritic region. Subsequently, when a highly segregated solidified alloy is exposed to

homogenizing-solutionizing temperature, incipient melting occurs in the interdendritic region. The poor microstructure resulting from uncontrolled solidification of the incipient melted regions makes the alloy unsuitable for the intended application. It is for this reason that the solidus temperature is the upper limit of the solutioning window [41, 42, 49].

It is commonly believed that the eutectic reaction takes place in the interdendritic region towards the end of solidification sequence. However, the very last stage of solidification of superalloys is not well understood. It is even proposed that a peritectic type reaction occurs in the interdendritic region before the γ - γ' eutectic reaction takes place [50]. In general, the eutectic temperature is the lowest temperature at which liquid exists in an alloy. However, it has been shown recently that due to high degree of segregation in superalloys, a small fraction of liquid exists in the interdendritic region even below the eutectic temperature. Hence, it is argued that complete solidification of superalloys takes place at a temperature much below the γ - γ' eutectic reaction [51]. It is also suggested that there is a possibility of up-hill diffusion occurring in heavily alloyed superalloys during extended holding leading to incipient melting in the interdendritic region [48, 52]. Consequently, it is very difficult to predict the onset of incipient melting during the homogenization-solution heat treatment of highly segregated superalloys. To overcome this problem of incipient melting, during homogenization-solution heat treatments, superalloys are frequently heated gradually in a series of temperature steps. At each temperature step, the alloy is increasingly homogenized so that the tendency for incipient melting is minimized.

However, this leads to extended homogenization-solution heat treatments that can be difficult to control.

Table 3.1 summarizes the standard step-wise homogenization-solution heat treatment for the third generation SX alloy, CMSX-10. The homogenization-solution step alone takes 45 h and involves 10 heating steps. The solution treatment is followed by 3-step aging heat treatment of 58 h holding time [41, 53]. This makes the total heat treatment cycle time about five days - a complex, tedious and very expensive process. Further, an analysis of the homogenizing-solutionizing behaviour of CMSX-10 concluded that “the development of a shorter or lower temperature optimized solution heat treatment is not likely” [41]. It is likely that this process would become more complicated and expensive for future generation alloys. Therefore, there exists an engineering challenge to study the heat treatment processes of SX superalloys rather critically leading to an improved understanding of the physical metallurgy processes controlling the homogenizing and solutionizing processes. Such an understanding will allow the design of more systematic and effective approach to homogenization-solution heat treatments. The original research and super-solidus processing presented in this thesis addresses this key issue.

4. Experimental Material and Procedures

4.1 Background

As mentioned in section 1.2 of this thesis, this research is a part of the on-going collaborative program between the Mechanical and Aerospace Engineering Department of Carleton University and the Institute for Aerospace Research (IAR), NRC. An initial phase of this program involved the commissioning of a pilot scale Bridgman furnace at Carleton University for casting high temperature materials such as superalloys and titanium aluminides in DS and SX forms [7]. After successfully installing the casting facility, this phase of the program included research aimed at understanding the heat transfer characteristics during the DS and SX casting processes in the Bridgman furnace [8]. As a result, a number of DS and SX bars of titanium aluminides and superalloys were successfully cast for subsequent research purposes.

A previous phase of this collaborative effort focused on studying the chemical composition effects on the microsegregation behaviour of superalloys during single crystal casting [9]. As outlined in Chapter 2, to improve SX superalloy high temperature capability there is a trend of increasing refractory metals additions, making recently developed alloys susceptible to microstructural and chemical instabilities. Therefore, a previous phase of this collaborative research effort studied the effect of individual refractory elements on the chemical segregation during DS

and SX alloy solidification [9-11]. In particular, the role of W, Re, and Ru on the microsegregation behaviour was determined by examining a set of six experimental superalloys with the carefully controlled nominal compositions shown in Table 4.1. Compositions of alloys A to D were set to study the variance of W and Re while maintaining the constant total refractory content at 21 wt%. Composition of alloy-E was designed to study the combined effect of high W and high Re. Alloy-F was specially designed to study the effect of Ru in a heavily alloyed superalloy. This previous phase of research has clearly established that an increased refractory content, especially increased concentration of Re, causes increased segregation and thereby increased eutectic fraction and increased heterogeneity in the DS/SX solidified microstructure [9-11]. It was also shown clearly that Ru significantly reduces the microsegregation and eutectic fraction in the solidified microstructure [11].

It should be noted from Table 4.1 that a significantly higher level of Ta (12 wt %) was added to the experimental alloys than is generally used in contemporary alloys (5-6 wt %). This was to ensure that the experimental alloys reached the solubility limit and, therefore, displayed high levels of segregation in the DS/SX solidified structure. Also, Ta is known to segregate to the interdendritic region [9-11, 54-56] and creates the balance in the densities of dendrite cores and interdendritic regions during solidification and thereby minimizes the convective currents between high and low density regions in the mushy-zone. This reduces the tendency to form defects such as freckles and spurious grains in the castings [55, 56]. Hence, better castability is ensured with a high Ta content.

4.2 Material Selection for the Present Thesis

The DSC thermal analysis performed in the previous research phases indicates very similar voltage change profiles and comparable phase transformation temperatures for all the experimental alloys, as shown in Figure 4.1 [9]. Hence, it is anticipated that the heat treatment response of all these alloys would also be similar. Therefore, the present thesis research focuses on a detailed homogenization-solutioning study on one of these experimental alloys. The conclusions can be extrapolated to the other alloys relatively easily. In principle, any one of the six experimental alloys could be selected for this research work. However, Alloy-B serves as an ideal representative of this alloy series since it contains a balanced refractory composition (2% W and 2% Re). Further, the as-solidified structure of Alloy-B exhibited the largest W partitioning ratio from the dendrite surface to the core [9-11]. Since W can be expected to be a slow diffusing element [54] these features make Alloy-B an ideal experimental material to meet the objectives of this research work.

4.3 Procurement of Experimental Material and Consumables

Alloy-B was supplied in the form of polycrystalline master alloy bars of 1.6 cm (5/8") diameter and 91 cm (36") length by a custom casting company, Sophisticated Alloys^{TM}, Pennsylvania, USA. After receiving the bars, the chemical compositions of the master alloys were confirmed by wet chemical analysis [9]. Figure 4.2 shows the master alloy bars in the as-received condition. Both nominal composition and the composition determined by wet chemical analysis are listed in the Table 4.2. As-received alloy bars were ground to remove the rough surface and cleaned with

acetone before using them for Bridgman processing. The rough ground master alloy and the consumables used for the mould preparations are shown in Figure 4.3.

Double open ended alumina tubes of inside diameter 1.6 cm, outside diameter 2.2 cm, and length 20 cm supplied by Vesuvius McDanel™ were used as the moulds (item 6 in Figure 4.3). To avoid the leakage of the melt in case of accidental mould failure during Bridgman processing, Mo foils were used to wrap the moulds (item 2 in Figure 4.3). Mo wires (item 1 in Figure 4.3) were used to tie the Mo foils at 3 different locations as shown in Figure 4.3 to ensure that the moulds are tightly wrapped so that cracks, if at all developed in the mould, will not open up easily. This is critical to prevent the leakage of liquid metal from the mould which can cause extensive and expensive damage to the Bridgman facility. Both the foils and wires of molybdenum were supplied by The Rembar Company, Inc., New York.

As the seed crystal method was adopted for Bridgman processing, single crystals of alloy PWA-1484 in the form of cylinders of about 2.5 cm height with the [001] direction oriented longitudinally were used as starter SX seed crystals (item 4 in Figure 4.3). Thoroughly inspected seed crystals were readily available, courtesy of the Institute for Aerospace Research, NRC with the nominal composition listed in Table 4.2. High purity alumina bars, supplied by Cotronics Ceramics, were sectioned to obtain cylindrical sections of 1.6 cm in diameter and 1.3 cm in height (item 3 in Figure 4.3). These alumina sections or spacers are placed at the bottom of the moulds to control axial heat transfer into the upper chill plate during Bridgman processing.

4.4 Bridgman Processing Procedure

The Carleton University Bridgman casting facility with accessories for power-supply, furnace controller, vacuum system and inert gas system is shown in Figure 4.4. A schematic of internal parts and major heat transfer modes within the furnace is illustrated in Figure 4.5. The furnace has a hot chamber with two tungsten heating elements within multilayer molybdenum heat shields. Retractable baffles made of zirconia board with a central hole separate the hot chamber and the cold chamber. The cold chamber has a water cooled copper chill plate for supporting the mould assembly which can be raised and lowered using a variable speed stepper motor system.

A detailed procedure for SX processing in the Bridgman furnace has been described in the earlier studies resulted from extensive experimental work [7-9]. In this work, the procedure optimized in the previous study is replicated with the only exception that argon is used instead of high vacuum as the inert medium in the Bridgman furnace. It was a concern in the previous casting practice that under high vacuum, volatile vapours released from the mould condensed on the internal surfaces of the vacuum pumps, and internal furnace components. To avoid such depositions and to protect the vacuum system, it was decided to maintain a positive pressure in the furnace and hence use argon as the inert medium and during Bridgman processing. In general, the standard Bridgman SX procedure involves four important stages: 1) prepare, load and raise the mould assembly into the hot chamber, 2) create an inert atmosphere in the furnace chamber using the vacuum systems and inert gas, 3) slowly

raise and hold the furnace hot chamber so that the alloy melts and attains a super heat temperature of 1585 °C, and 4) withdraw the mould assembly from the hot chamber into the cold chamber at an optimized rate of 20 cm/h.

For loading and unloading the mould, the cold chamber has a rectangular door with a hinged shutter as shown in Figure 4.6. The mould wrapped with Mo foil is loaded on the top of the copper chill plate with the help of a mould holder as shown in Figure 4.7. The mould is then filled with alumina spacer, seed crystal, and alloy bars in that order as illustrated in Figure 4.3. The chill plate is then slowly raised so that the mould enters the hot chamber without touching the baffles and stops at a predetermined position with the bottom of the starter seed crystal inline with the zirconia retractable baffles.

After confirming the correct position of the mould assembly, the cold chamber door is closed tightly so that a vacuum can be maintained in the furnace. The *rough* vacuum is first preformed using only the mechanical vacuum pump. The residual air inside the chamber is then diluted by purging with high purity argon gas. A *high* level vacuum is then attained and maintained using both mechanical and diffusion pumps.

Once the required vacuum is attained, the power supply to the furnace heating elements is switched on and the furnace temperature is raised slowly following the thermal profile shown in Figure 4.8. To minimize the thermal stresses in the heating elements and other furnace components and to ensure a smooth operation, the furnace

temperature is brought to 100 °C using manual control with a heating rate of approximately 2 °C/min followed by programmed heating rate of 10 °C/min up to 500 °C and 20 °C/min up to 1585 °C.

Once the required superheat temperature is reached, the furnace is back-filled with argon and a positive pressure of about 27.6 kPa is maintained inside the furnace chamber. To ensure complete homogenization of the liquid alloy, the mould is held in this position prior to initiating withdrawal for 15 minutes. The withdrawal of the mould into the cold chamber is then started at 20 cm/h while maintaining the argon inert atmosphere and the hot chamber temperature at 1585 °C. Figure 4.9 is a schematic of the hot chamber showing the arrangements of the heating elements, mould position and the furnace control thermocouple. It has been established in earlier studies that the superheat temperature of the alloy in the mould is approximately 1625 °C when the hot chamber temperature is 1585 °C [7, 8].

Proper positioning of the mould assembly prior to withdrawal ensures that alloy is completely melted while the seed crystal is only partially (top 1/8) melted which is the ideal condition for the SX processing. The temperature profile set up within the mould as established in earlier experimental studies [9] and ProCast simulations [8] is shown in Figure 4.10. The major heat transfer modes set up during the mould withdrawal are illustrated in Figure 4.11 [8]. Once the mould is completely withdrawn into the cold chamber, the furnace temperature is cooled using the thermal profile shown in Figure 4.8. The furnace is initially cooled at a slower rate of

25 °C/min. The power supply to the heating elements is cut off at 1000 °C and the furnace is cooled naturally. A sample of the recorded chart of the furnace and the coolant water temperatures is provided in Figure 4.12. Once the temperature of the furnace is below 100 °C, the chamber pressure is released, the cold chamber door is opened and the mould is removed. The SX casting is then removed by breaking the mould as shown in Figure 4.13. Though the previously optimized SX procedure was followed for the most part, the following improvements and contributions were made during the present research work:

1. SX processing in an argon atmosphere was successfully established with significant improvements in SX quality. After performing a number of casting trials it was clear that argon backfilling prior to melting the alloy, traps the gas at the alloy-mould interface and hence creates *blowholes* on the casting surface. If argon is backfilled after the alloy has been completely melted there cannot be any interface clearance between the mould and the melt, hence there is no possibility of gas entrapment and subsequent formation of *blowholes*. The improvement to the quality of the SX cast bars is shown in Figure 4.14.
2. It was understood from earlier processing practices that a wide clearance between the mould and seed crystal allows liquid metal seepage into this clearance which on solidification nucleates spurious grains. In addition, during the current this research work it was determined that this procedure also allows surface contamination and results in a defective patchy surface on

the casting, as shown in Figures 4.14 and 4.15. Hence, both seed crystal and alumina spacer must be machined to a diameter that only just allows insertion into the alumina mould providing for a tighter tolerance fit than previously employed.

4.5 Metallography of Bridgman Processed Bars

To study the SX structure, Bridgman processed bars were sectioned transversely at different locations. These sections were ground and polished to 0.1 μm finish using a series of abrasive papers as per standard metallographic procedures. The specimens were then cleaned thoroughly using alcohol bath in an ultrasonic cleaner. To study the extent of micropores, the specimens were observed in stereomicroscope before etching. The specimens were then etched in a solution of 10 ml HCl, 10 ml HNO_3 , 0.3 g molybdic acid, and 15 ml H_2O to study various features of as-solidified microstructure.

4.6 Homogenization-Solution Heat Treatments

To obtain a comprehensive understanding of the heat treatment response, four different types of heat treatments were designed and applied to the experimental Bridgman processed Alloy-B bars.

4.6.1 Stepwise Homogenization-Solution Heat Treatments

The Bridgman processed Alloy-B SX bars with the longitudinal axes along $\langle 001 \rangle$ were sectioned in the transverse direction to obtain discs that were approximately

6 mm in thickness. These discs were further sectioned longitudinally to obtain half moon shaped specimens. A box type radiant furnace with accurate temperature control of ± 1 °C was used for heat treatments. An additional thermocouple with its bead in contact with the specimen was used to confirm the temperature measurement. Table 4.3 lists stepwise heat treatment experiments in which each temperature step follows in sequence. A temperature range of 1170 to 1320 °C was chosen based on the DSC thermograph of the alloy shown in Figure 4.1. It is clear from the DSC profile that there is no phase transformation occurring in the alloy up to about 1180 °C. Therefore, the specimens were heated quickly to 1170 °C by inserting them into the furnace which was already heated and stepwise holding with increased temperature was followed thereafter. In general, the hold time steps were designed to study the effect of extended holding at various temperatures as illustrated in Figure 4.16. To track the microstructural evolution during the stepwise heat treatments, specimens were quenched in water after each step. All the experiments were performed in an air atmosphere. To avoid the interference of surface oxidation in the analysis, the specimen discs were sectioned transversely at the centre of 6 mm thickness and the unoxidized surfaces were used for metallographic examination. Specimens were prepared for optical microscopy by grinding to 1 μm finish using standard metallographic procedures, followed by etching in a solution of 0.3 g molybdic acid, 10 ml HNO_3 , 10 ml HCl and 15 ml H_2O . The results of the stepwise homogenization-solution heat treatments are presented in Chapter 5.

4.6.2 Continuously Heating Homogenization-Solution Heat Treatments

The continuously heating experiments were designed after some basic phase transformation information of the alloy was obtained from the stepwise heat treatments. However the objective of these experiments was to study the effects of continuous heating between the solvus and solidus temperatures and compare the results with isothermal steps described in the stepwise heat treatments. The temperature ranges and heating rates programmed in the furnace controller are shown in Table 4.4 and Figure 4.17. As the smallest control interval of the furnace is 1 °C, the so called continuous heating between the chosen temperature ranges was actually stepwise heat treatment with small 1 °C increments. For example, in experiment CH1, step size between 1285 and 1310 °C was 1 °C/1h. Similarly, in experiment CH4, step size was 1 °C/4h between 1295 and 1305 °C. The specimens were inserted into the furnace which was already heated to the lower temperature followed by further heating at a controlled rate. Once the higher temperature was attained, the specimens were cooled quickly by quenching in water. The metallography of the quenched specimen was followed as described in the section 4.6.1. Results and discussion of the continuously heating experiments are provided in Chapter 5.

4.7 Super-Solidus Heat treatments

4.7.1 Short Exposure Experiments

The purpose of the short exposure heat treatments was to trace the solidification sequence of the SX alloy by tracking the microstructure variation within the wide temperature range of 1250 °C to 1360 °C – with emphasis on temperatures above the

solidus. Specimens conforming to the same geometry as previously described were held isothermally for 2 hours at various temperatures shown in Table 4.5 followed by water quenching. To study the effects of slower cooling rate, one of the specimens, SE9 in Table 4.5, was cooled in still air. The specimens were then subjected to the standard metallographic analysis as described earlier. Results of the short exposure heat treatments are discussed in Chapter 6.

4.7.2 Super-Solidus Homogenization-Solution Heat Treatment

Table 4.6 describes the super-solidus homogenization-solution heat treatment. The unique theme of the super-solidus heat treatment was to expose the solidified Alloy-B to a temperature in excess of the solidus (the 1350 °C step in Table 4.6) followed by quenching so as to obtain a refined microstructure. The super-solidus exposure was followed by a regular sub-solidus stepwise heat treatment as shown schematically in Figure 4.18. Results of super-solidus heat treatments are also discussed in Chapter 6

4.8 Super-Solidus Processing in Bridgman Furnace

In these experiments, the super-solidus portion of the heat treatment described in section 4.6.4 is incorporated as a modification to the Bridgman SX processing cycle. This method possessed an additional super-solidus step following the usual Bridgman processing steps. The procedure included the following steps:

1. solidify a SX superalloy bar conventionally in a Bridgman furnace,
2. reduce the furnace temperature to an appropriate mushy-zone temperature,

3. raise the mould assembly back into the furnace and hold at the mushy zone super-solidus temperature, and
4. withdraw the mould assembly rapidly for quick re-solidification.

To accommodate this additional super-solidus step, the furnace temperature profile illustrated in Figure 4.19 was programmed. To optimize the super-solidus temperature and the withdrawal rate after the super-solidus exposure, several experiments listed in Table 4.7 were performed. A sample of the recorded chart of furnace temperature versus time, showing the additional super-solidus step is shown in Figure 4.20. The super-solidus processed specimen obtained by the optimized experimental condition was subjected to a simple shortened three temperatures-six hour stepwise heat treatment described in Table 4.8. Results are discussed in Chapter 7.

4.9 Characterization

4.9.1 Metallography

All the experimental specimens were analyzed by the standard metallographic procedures outlined in the foregoing sections. The specimens were observed using an optical microscope before and after etching to study the porosity and microstructural features as described in section 4.5.

4.9.2 Eutectic Phase Fraction Analysis

To track the degree of solutionizing, the eutectic phase fraction was determined by using the image analysis software, Image Tool ^{TM}. A representative low magnification optical micrograph of the alloy obtained after each heat treatment step was converted

into 16-bit grayscale format. After adjusting the brightness and contrast to delineate the dendrite and eutectic region, the grayscale format was converted into black and white threshold image using an Image Tool™ subroutine. Residual pixels corresponding to the eutectic region present in the black and white images were removed manually using a pixel editing tool. Finally, areas corresponding to dendrite and eutectic regions were obtained by counting the pixels from the black and white regions.

4.9.3 Electron Probe Microanalysis (EPMA)

It has been established that a sharp compositional gradient exists in the solidified alloy from the interdendritic eutectic to dendrite core region along [011] type direction [26]. Hence, studying the variation of this composition profile after each heat treatment step gives an estimate of the degree of homogenization and hence the effectiveness of the heat treatment step. To study the variation of composition profiles, a series of spot chemical analysis were performed with intervals of about 25 μm along a line from the eutectic region to the dendrite core. A Camebax Electron Microprobe with Wavelength Dispersive X-Ray (WDX) spectrometers was used for the analysis. All the parameters including the equipment, operator, calibration procedure, specimen preparation procedure, measurement procedure were replicated from the earlier work [9]. Selected specimens ground to 1 μm finish by standard metallographic techniques were used for the analysis. The electron probe with accelerating voltage of 20 kV and beam current of 35 nA was used for the analysis over 5 μm x 5 μm raster with total counting time of 60 s for each element. A well

characterized suite of pure metals and minerals was used for calibration. The matrix correction software, Cameca PAP, was used for converting X-ray data into elemental weight percent. The limits of background noise levels were carefully determined by running wavelength scans on either side of the peak position of each analyzed element. As a result, reliable quantitative results were obtained including the refractory elements added in small amounts (Appendix-A). It has been confirmed that measurement error for Ni, Al, Cr, Ta and Co is less than 1 % while error for Re, Ti and W is about 7 % of the measured value (Appendix-B).

5. Homogenization-Solution Heat Treatments

In this chapter, results of stepwise homogenization-solution heat treatments from Table 4.3 are presented first. The purpose of these experiments is to study the effect of the conventional stepwise homogenization-solution sequence on the microstructural homogeneity. As the solidus temperature is the upper limit for conventional stepwise homogenization-solution heat treatments, microstructural evolution is governed by the sub-solidus temperature steps. Therefore, for the most part, experiments were terminated when specimens exhibited the onset of incipient melting as determined by microstructural examination. As mentioned in section 4.6.1, these experiments are designed in such a way where one holding time step in each experiment is significantly extended compared to the rest of the heat treatment steps (Figure 4.15). Hence, the influence extended hold time step at low, intermediate and high temperatures on the homogenization-solutioning behaviour of the alloy can be clearly understood. Beneficial findings of the stepwise heat treatments are applied to the continuous heating homogenization-solution heat treatments listed in Table 4.4, and the results are presented later in this chapter.

5.1 Microstructural Analysis

The solidified microstructure of the alloy is shown in Figure 5.1. As expected, the alloy exhibits a highly segregated dendritic structure with primary and secondary dendrite arms oriented along $\langle 001 \rangle$. All the microstructural features, including the precipitation of fine γ' within the dendrites, the presence of cellular eutectic γ - γ' in

the interdendritic region, and primary dendrite arm spacing (PDAS) of about 250 μm , are consistent with the results obtained in the earlier work for the alloy [9].

Figure 5.2 shows the microstructural developments during the stepwise heat treatment identified as experiment SW1 in Table 4.3 that possesses a low temperature extended time step of 15 h at 1170 °C. Figure 5.2a indicates that there is no notable change in the microstructure of the alloy as a result of extended hold time at 1170 °C step. The first visible signs of microstructural change occur during the 1250 °C step where the interdendritic region around the eutectic phase becomes denuded of fine γ' precipitates (Figure 5.2b), indicating that solutioning begins in the interdendritic regions. This microstructural change correlates well with the DSC profile of the alloy (Figure 4.1) where small peak in the vicinity of 1200 °C is observed. This result is also consistent with the observation reported by the other workers [26]. However, during the higher temperature hold time steps, this γ' denuded region does not extend into the dendrites. Instead, dendritic solutioning begins in the dendrite core region first during the 1280 °C holding time step (Figure 5.2c), followed by complete solutioning of dendrites during the 1300 °C hold time step leaving behind the undissolved eutectic in the interdendritic regions (5.2d). During the 1310 °C step the onset of incipient melting occurs in the interdendritic region adjacent to the residual eutectic (Figure 5.2e). Based on these observations it may be inferred that the solvus temperature of the alloy is approximately 1290 °C.

Figure 5.3 illustrates the effect of adding an intermediate temperature extended hold at a sub-solvus temperature of 1280 °C/5 h (experiment SW2). The direct effect of

this added extended hold time at a sub-solvus temperature of 1280 °C is clearly visible after an additional hold time step at 1310 °C. While there is no indication of the onset of incipient melting, the microstructure (Figure 5.3a) is more homogenized than in Figure 5.2d (the same heat treatment without the extended hold time at 1280 °C). The lack of incipient melting of the alloy subjected to 1280 °C confines up to 1315 °C (Figure 5.3b). However, during the 1320 °C step the alloy displays signs of incipient melting (Figure 5.3c). The microstructure after 1325 °C (Figure 5.3d) confirms that incipient melting occurs at both interdendritic regions and within the dendrites. These results indicate that the extended hold at 1280 °C imparts greater homogenization of the microstructure and increases the incipient melting temperature from 1310 °C to 1320 °C.

Figure 5.4 provides a summary of the microstructural development of the experiment SW3, with a 15 h hold at 1280 °C. As observed in the earlier experiments (SW1 and SW2) that there is no noticeable microstructural change during the 1170 °C exposure (Figure 5.4a). Further, dissolution of fine γ' around the eutectic is consistent with the microstructural observation after 1250 °C (Figure 5.4b). Microstructures after 1280 °C, 1300 °C and 1310 °C steps (Figures 5.4c, 5.4d and 5.4e) reveal a systematic solutioning of dendrites. However, it is clear that even with further extension of hold time at 1280 °C (15 h) the occurrence of incipient melting at 1320 °C is persistent (Figure 5.4f).

Figure 5.5 compares the microstructures of the alloy after 1280 °C hold for 2, 5 and 15h from the experiments, SW1, SW2 and SW3 respectively. The microstructures

indicate an increasing trend in the eutectic fraction with the extended hold time at a sub-solvus temperature. It should be noted that in SW3, the alloy was held at 1170 °C for only 2 h as compared to 15 h in SW1 and SW2. However, there is no transformation or microstructural change taking place at this temperature (Figures 5.2a, 5.4a). Hence, the microstructural change in Figure 5.6 is due to the extended holding at 1280 °C. From the microstructural results of experiment SW1, SW2 and SW3 it may be stated that extended holding at a sub-solvus temperature increases the onset of incipient melting marginally, but stabilizes the eutectic phase. In other words, sub-solvus temperature holding steps contribute to homogenization, but do not help in solutioning the alloy.

By comparing Figures 5.4f and 5.3c it can be noted that the occurrence of incipient melting at 1320 °C is consistent and similar in nature. This display of microstructural change is indicative of an invariant reaction taking place at 1320 °C. Comparison of high magnification microstructures of the alloy, before and after the 1320 °C step, confirms that the residual eutectic blocks in the interdendritic region melt and solidify into cellular colonies as illustrated in Figure 5.6. These colonies are smaller in size, but appear similar to the cellular γ - γ' eutectic in the as-solidified microstructure shown in Figure 5.1b. This observation indicates that the alloy undergoes a eutectic reaction at 1320 °C, and that the complete solutioning of the alloy should be completed before reaching this temperature. However, experiment SW4 revealed incipient melting after prolonged holding at temperatures 1315 °C as shown in Figure

5.7. Furthermore, experiment SW5 displays a systematic progression of incipient melting during extended holding at 1310 °C as shown in Figure 5.8.

Figure 5.9 shows the results of experiments SW6 involving extended holding at 1305 °C. A systematic reduction in the eutectic volume fraction is evident from the micrographs indicating that γ' solutioning is very effective at higher temperatures. However, Figure 5.9d indicates the onset of incipient melting and hence confirms the deleterious effect of prolonged holding beyond a certain hold time.

From the foregoing observations, it is clear that there is an incubation time for the onset of incipient melting during a temperature step above solvus. At 1305 °C holding temperature, the incubation time is between 10 h and 20 h. Experiments SW1 to SW5 further show that depending on the lower temperature steps, incubation time at 1310 °C lies within 5 h limit. From experiments SW2 and SW3, it is also clear that the incubation time at 1320 °C is within 2 h. This indicates that the incubation time for incipient melting decreases with an increase in temperature as shown by the incipient melting map in Figure 5.10. In other words, the incipient melting temperature is a variable that is controlled by the degree of homogenization of the alloy. It is thus safe to state that, after completely homogenizing the alloy, the onset of incipient melting should reach the equilibrium solidus temperature of the alloy that remains a constant. In Figure 5.10, the line that connects the onset of incipient melting reaches a temperature slightly below 1305 °C indicating that the equilibrium

solidus temperature of the alloy should be close to 1305 °C. For all practical purposes, it may be approximated that the solidus temperature of the alloy is 1305 °C.

Based on the microstructural observations, it may be summarized that γ' - solvus, equilibrium solidus and eutectic temperatures of the alloy are 1290 °C, 1305 °C, and 1320 °C respectively. Hence, the solutioning window for the alloy is approximately 15 °C between 1290 °C and 1305 °C. The results further indicate that prolonged sub-solvus holding (1280 °C/2h, 5h, and 15h) promotes homogenization and raises the solidus temperature marginally. In addition, prolonged holding at a sub-solvus temperature also stabilizes eutectic, and hence, does not promote solutioning. The microstructural results also indicate that, γ' solutioning is effective within the solutioning window and that irrespective of the degree of homogenization or the thermal history of the alloy, extended holding at and above equilibrium solidus temperature leads to incipient melting.

5.2 Eutectic Phase Fraction Analysis

Results of eutectic phase fraction analyses performed on selected specimens are summarized in Table 5.1. Figure 5.11a and 5.11b illustrate the effects of extended holding on the solutioning at a sub-solvus temperature (1280 °C) and a super-solvus temperature (1305 °C) respectively. Figure 5.11c shows the effect of stepwise increase in the temperature within the solution window of the alloy.

As indicated in Figure 5.11a there is a trend of increasing eutectic fraction with an increase in the holding time at 1280 °C. This implies that an extended holding at a sub-solvus temperature stabilizes the eutectic phase rather than dissolving it. This quantitative analysis confirms the microstructural observations of Figure 5.6. Clearly, extended holding above the solvus temperature shows a systematic reduction in the eutectic fraction (Figure 5.11b). The stepwise heat treatment with increase in the holding temperature also shows a monotonic reduction in the eutectic phase as shown in Figure 5.11c. This indicates that a sub-solvus heat treatment has no beneficial effect on the dissolution of the eutectic phase while a super-solvus heat treatment is beneficial.

5.3 Electron Probe Microanalysis (EPMA)

An illustration of the location of EPMA measurements from the eutectic region to the dendrite core is shown in Figure 5.12. The complete microprobe data are listed in Appendix-A. For clarity, composition profiles of selected elements after heat treatment steps in experiment SW6 are shown in Figures 5.13 and 5.14. These elements are selected as they serve as representative examples of elements showing strong segregation behaviour to dendrite cores (Re, Cr) and interdendritic regions (Ta, Ti). As evident from Figures 5.13 and 5.14, there is a sharp gradient in elemental concentrations between the eutectic and the dendrite core regions. The profiles in Figure 5.13 show that the eutectic to core gradient decreases with an increase in the heat treatment temperature. This is indicative of increasing homogenization with an increase in temperature. Conversely, profiles in Figure 5.14 show an increase in the

eutectic to core gradient with increase in holding time at 1305 °C. This suggests that the degree of segregation increases with prolonged holding at 1305 °C.

The degree of homogenization can be expressed as the difference between the maximum point and the minimum point in the elemental concentration profile. Lower the difference, flatter the profile, more homogeneous the alloy. Table 5.2 lists the variation in the degree of homogenization with increasing holding temperature and time. There is a clear trend of increased homogenization with increasing heat treatment temperature from as-solidified structure to heat treated structure up to 1305 °C/2 h. In contrast, prolonged isothermal holding at 1305 °C from 2 h up to 20 h leads to an increase in the microsegregation of every element.

After heat treatment the composition profiles within the dendrite portions in Figures 5.13 and 5.14 are relatively flat and smooth. It is clear that the dendrite core quickly homogenizes with an increase in temperature and attains a composition that is closer to the nominal composition of the alloy. Further, the core also remains homogenized during extended isothermal holding. However, during prolonged isothermal holding, the eutectic region diverges significantly from the nominal composition of the alloy (Figure 5.14). Such an unusual behavior in the eutectic region has been described as up-hill diffusion during which elements diffuse “up” the compositional gradient to the regions of higher concentration [52]. Importantly, the present work confirms that up-hill diffusion indeed occurs and leads to incipient melting during long isothermal holding (Figure 5.8, 5.9). The EPMA results also confirm that stepwise heat treatment

with progressively increasing temperature is more beneficial in terms of homogenization than the isothermal heat treatment. Hence, a stepwise heat treatment between solvus and solidus temperatures provides an effective solutioning approach. As evident from the results presented, this solutioning window is generally narrow for superalloys with high refractory content. Hence, a stepwise heat treatment within the narrow temperature window would also require a large number of increment temperature steps for effective solutioning. Hence, a slow and continuous heating may prove to be a better practical solutionizing method.

It is discussed in section 5.1 that there is a finite incubation time for the onset of incipient melting at a specific temperature. It is clear now from the EPMA results that the incubation time for incipient melting is controlled by the up-hill diffusion in the interdendritic region. The higher the temperature, the faster the up-hill diffusion, and hence, the quicker the onset of incipient melting. This information can be utilized in designing efficient continuous heating experiments within the available solution treatment window (1290 °C -1305 °C). As the incubation time is longer for lower temperatures and shorter for higher temperature, the heating rate should be such that the total exposure time at any temperature is within the incubation time limit. Hence, continuously increased solutioning without causing any incipient melting can be achieved.

5.4 Continuous Heating Experiments

The results of continuous heating experiments are summarized in Table 5.3, and corresponding microstructures are presented in Figure 5.15. The continuous heating experiment CH1 displays incipient melting (Figure 5.15a). However, the rest of the experiments, CH2 to CH4 show improved solutioning without any signs of incipient melting.

The incipient melting in experiment CH1 occurs because specimen exceeds the solidus temperature of 1305 °C. In contrast, the specimens in CH2 to CH4 experiments were quenched at 1305 °C before the onset of incipient melting. The minimum residual eutectic achieved in the stepwise heat treatment (SW6) is about 1% after the isothermal heating at 1305 °C for 20h, Table 5.1. However, it should be noted that there were signs of onset of incipient melting (Figure 5.9d). In contrast, continuous heating within the solutionizing window seems quite successful in avoiding incipient melting even after 40 hours of heating between the solvus and the solidus temperatures and the residual eutectic content was as low as 0.5% (Table 5.3).

5.5 Conclusions

The heat treatment response of an experimental SX superalloy studied by heat treatments between 1170 to 1325 °C may be summarized as follows:

- Approximate solvus, equilibrium solidus, and eutectic temperatures of the alloy are estimated to be, 1290 °C, 1305 °C, and 1320 °C respectively.

- Sub-solvus homogenization heat treatments help in marginally raising the incipient melting temperature of the alloy.
- Extended isothermal hold time at a sub-solvus temperature has no beneficial effect on the dissolution of the eutectic γ' phase.
- Extended hold time at and above the solidus temperature leads to incipient melting, irrespective of the thermal history of the alloy during the heat treatment.
- Heat treatment between solvus and solidus temperatures homogenizes the dendrite core quickly. However, up-hill diffusion occurs in the eutectic regions during isothermal holding that leads to incipient melting.
- Continuous heating at a slow heating rate between the solvus and solidus temperature promotes complete solutioning and homogenization of the alloy without causing incipient melting.

A new solutioning-homogenizing heat treatment scheme, compared to the usual traditional stepwise heat treatment sequence, shown in Figure 5.16 is proposed. The procedure for designing an effective homogenizing-solutioning heat treatment for a newly designed alloy with heavy refractory content would be as follows:

1. quantify the heat treatment temperature range of interest from the DSC thermograph of the alloy,
2. determine the approximate solvus and solidus temperatures using stepwise heat treatments with increasing temperature and a constant hold time step of 2 h,
3. quickly raise the temperature of the specimen to the solvus temperature,
4. heat the specimen at a slow rate of about 1 °C/h, and
5. quench just before reaching the solidus temperature.

6. Super-Solidus Heat Treatments

As discussed in the literature review sections 3.3 and 3.4, homogenization-solution heat treatments are limited to sub-solidus temperatures so that incipient melting is avoided. Likewise, one of the criteria for suitability of the heat treatments presented in the previous chapter was the occurrence of incipient melting. Due to the microstructural damage caused by incipient melting, the homogenization-solution heat treatments for commercial superalloys are designed to be sub-solidus. However, if the extent of incipient melting were to be carefully controlled, and if heat treatment were appropriately designed so that the incipient melted regions re-solidified with a controlled and desirable microstructure, then it may be possible during homogenization-solution heat treatment to apply temperatures higher than the solidus - in essence, a *super-solidus* homogenization heat treatment. Results presented and discussed in this chapter explore the potential for super-solidus heat treatment.

The previous chapter approximates the solidus temperature of the alloy at 1305 °C. Though, focus of the study in this chapter is on super-solidus exposures, for studying the response of the alloy over a wide temperature range, short thermal exposure experiments shown in Table 4.5 involving both sub-solidus exposures (SE1, SE2) and super-solidus exposures (SE3-SE9) are performed. The results of these experiments are discussed in section 6.1. Important findings of these experiments are used in designing the super-solidus homogenization-solution heat treatment shown in Table 4.6 and the results are presented in section 6.2.

6.1 Short Exposure Heat Treatments

Figure 6.1 shows the microstructures of the specimens exposed to temperatures, 1250 °C and 1300 °C (SE1 and SE2 from Table 4.5). Consistent with the earlier results the region surrounding the eutectic is denuded of γ' after 1250 °C exposure (6.1a). The dissolution of dendritic γ' in the γ matrix can be observed from the bright dendrite core regions of the specimen exposed to 1300 °C (Figure 6.1b). From SE1 and SE2 experiments, it is also clear that no incipient melting takes place up to 1300 °C.

Figure 6.2 summarizes the microstructural change of the specimens exposed to 1310 °C to 1360 °C (SE3 to SE8 from Table 4.5). In the specimen exposed to 1310 °C, incipient melting occurs in the interdendritic region while adjacent eutectic phase remains intact (Figure 6.2a). However, the specimen exposed to 1320 °C reveals the melting and re-solidification of the eutectic phase in the interdendritic regions (Figure 6.2b). The presence of enlarged and isolated interdendritic liquid zones that subsequently solidify is apparent from the microstructure of the specimen quenched from 1330 °C (Figure 6.2c). The microstructure of the specimen quenched from 1340 °C indicates that the isolated pockets of interdendritic liquid solidify into very fine 're-solidification' dendrites (Figure 6.2d). The microstructure of the specimen quenched from 1350 °C shows a larger fraction of the re-solidification dendrites that form from the interdendritic liquid within the network of parent dendrites (Figure 6.2e). An important feature of this microstructure is that there is crystallographic directionality in the growth of these re-solidification dendrites.

It is apparent from Figures 6.2d and 6.2e that the re-solidification dendrites grow along $\langle 001 \rangle$ and hence mimic the SX structure of the parent material. This epitaxial growth would be expected if the specimen was subjected to directional cooling, as in the case of SX growth using the Bridgman method, but in these short exposure heat treatments, the specimens were quenched in water and hence underwent omnidirectional cooling through the entire surface of the specimens. It is apparent from Figure 6.2e that the re-solidification dendrites grow from the surfaces of the secondary arms of the parent dendrites. As the internal solid surfaces act as nuclei or seed crystals with an orientation of $\langle 001 \rangle$, the re-solidification dendrites must have grown coherently along $\langle 001 \rangle$, despite omnidirectional heat removal during quenching.

Figure 6.2f indicates that during the 1360 °C exposure most of the specimen has melted, except the primary dendrite cores, and during subsequent quenching the $\langle 001 \rangle$ directionality is lost as indicated by the random orientation of the re-solidification dendrites. It was noticed while removing this specimen from the furnace that 1360 °C exceeds the mechanical softening temperature resulting in a loss of structural integrity. The quenched specimen, although distorted, was still used for the microstructural observation. It is most likely that the mechanical distortion caused by handling of the specimen during quenching affected the crystallographic orientation of the primary dendrite cores. It is most likely that the disturbance of the SX structure of the parent material affected the directionality of the re-solidified structure.

The foregoing observations make one point clear: $\langle 001 \rangle$ directionality of the re-solidification dendrites can be retained as long as the parent dendrites remain interconnected at the heat treatment temperatures, providing $\langle 001 \rangle$ oriented heterogeneous nucleation sites for the fine dendrites and favorable directional growth of these resolidified dendrites along the primary cubic directions (i.e. parallel and perpendicular to the secondary arms). Although this phenomenon of coherent SX growth is observed in this experimental superalloy, it is reasonable to expect that this phenomenon is generic in nature and could occur in commercial SX alloys as well. The optimum temperature for such a favourable condition may differ depending on the chemistry of the alloys. For the experimental alloy used in this research, the optimum super-solidus heat treatment temperature is likely between 1340 °C and 1350 °C.

Figure 6.3 compares a regularly solidified SX specimen with those re-solidified from 1340 °C, 1350 °C, and 1345 °C (experiments SE6, SE7 and SE9 from Table 4.5). It is clear that the dendrite core region remains solid throughout those heat treatments, but interdendritic region transforms into the resolidified structures. Comparison of Figure 6.3a and 6.3b indicates that the super-solidus heat treatment causes the coarse interdendritic region of the solidified structure to re-solidify into a fine morphology since the resolidification dendrites originate from the parent dendrites and grow into the interdendritic liquid. In other words, this super-solidus exposure followed by quick cooling transforms the interdendritic region without affecting the SX structure and gives rise to a fine resolidified interdendritic microstructure.

It should be noted however, that the specimen exposed to 1345 °C was held for only 0.5 h and cooled slowly in still air, while the specimens exposed to 1340 °C and 1350 °C were held for 2 h and cooled quickly by quenching in water (SE7 and SE9 in Table 4.5). The microstructures reveal that the coherent SX growth of the fine resolidification dendrites is repeatable even during slower cooling in air. Comparison of Figure 6.3c and 6.3d suggests that the size and morphology of the re-solidification dendrites vary slightly. Though faster resolidification gives rise to a finer structure, the directionality of the re-solidification dendrites is unaffected by a shorter exposure time (0.5 h) and the slower air cooling rate.

In the conventional stepwise homogenization-solution heat treatment of SX superalloys, the dissolution of the blocky interdendritic eutectic γ' phase in the γ matrix is a cumbersome and a time consuming process [41, 48]. In contrast, the formation of directionally favorable re-solidification dendrites using a suitable super-solidus heat treatment essentially amounts to effective mixing of the interdendritic region in the liquid state without affecting the overall SX structure. During this process, the bulky eutectic phase is redistributed into thin sections between the re-solidification dendrites. This resolidified structure yields a finer and greatly reduced eutectic fraction as illustrated in Figure 6.4. As there is an increase in the surface area of eutectic γ' phase, such a morphology should be easier to homogenize. To confirm this, a specimen was subjected to a *super-solidus* temperature of 1350 °C followed by the stepwise homogenization-solution heat treatment shown in Table 4.6. The results are presented in the following section.

6.2 Super-Solidus Homogenization-Solution Heat Treatment

The microstructural change occurring during the super-solidus homogenization-solution heat treatment (Table 4.6) is presented in Figure 6.5. The specimen after the super-solidus step (1350 °C/2 h/WQ) shows a SX structure with <001> oriented resolidification dendrites (Figure 6.5a). A homogeneous microstructure with no blocky eutectic is seen in after 1250 °C step (Figure 6.5b). Following the 1300 °C step, most part of the specimen is solutionized except thin sections between the resolidification dendrites. These continuous sections become discrete during the 1310 °C step (6.5c) indicating a higher level of solutioning. After 1320 °C step however, the alloy displays interdendritic incipient melting.

A set of high magnification microstructures focusing on the interdendritic region, is shown in Figure 6.6. The morphology of the resolidification dendrites is clear in Figure 6.6a. Three different structures distinctly seen are: 1) grey resolidification dendrites, 2) bright cellular structure ahead of the resolidification dendrites, and 3) fine and dark structure around the dendrite arms. A detailed characterization is required to clearly understand these structures. However, given the fact that alloy has only two phases (γ and γ') and underwent only a short exposure heat treatment, it is likely that these resolidification structures are composed of γ and γ' phases. Figure 6.6b illustrates how the resolidified structures are modified during the 1250 °C exposure step. It should be noted that 1250 °C is below the solvus temperature (1290 °C) of the alloy. Essentially, during this step the alloy underwent a sub-solvus precipitation heat treatment. The precipitation of γ' within the re-solidification

dendrites is very clear. By comparing the image contrast between the γ' precipitate and the γ matrix, it appears that the region ahead of the resolidification dendrites is γ and the structure surrounding the dendrite is coarse γ' .

The microstructure after the 1300 °C hold step is shown in Figure 6.6c. It should be noted that 1300 °C is a super-solvus temperature and the microstructure indicates the dissolution of fine γ' precipitates within the resolidification dendrites. The γ' sections between the resolidification dendrite arms remain undissolved. However, during 1310 °C holding, indications of partial solutioning is apparent from the discretization of γ' sections within the continuous matrix (Figure 6.6d). Formation of cellular phase in the interdendritic region (Figure 6.6e) confirms that the specimen experienced incipient melting during 1320 °C step. Considering that the eutectic temperature of the alloy is 1320 °C, it is likely that the residual undissolved sections of γ' and the surrounding γ' matrix underwent eutectic reaction and formed the cellular structure. It is conceivable that complete dissolution of γ' would occur with slightly extended holding time at 1310 °C.

Figure 6.7 compares the microstructure of the specimen after the 1310 °C hold step and homogenization-solution heat treated microstructure of a polycrystalline superalloy [57]. The absence of any dendrite boundary in the interdendritic region and presence of discrete sections of undissolved γ' and the continuous matrix across in Figure 6.7a is significant as it indicates that the crystallographic orientations of

adjacent dendrites match, and hence, the SX structure of the alloy specimen remains unaffected by the super-solidus homogenization-solution heat treatment.

6.3 Conclusions

The super-solidus heat treatments of SX superalloy has been studied by holding the alloy at various temperatures above and below the solidus temperature. The following conclusions are drawn from the results.

- The phenomenon of epitaxial SX growth during re-solidification of SX superalloys from a super-solidus temperature was identified and investigated. This phenomenon is characterized by the formation of colonies of very fine re-solidification dendrites within the interdendritic regions of the parent dendrites that are oriented along the $\langle 001 \rangle$ directions.
- The favourable condition for promoting directional growth of the resolidification dendrites was identified to be the presence of interconnecting secondary dendrite arms at the super-solidus heat treatment temperatures.
- An important concept for super-solidus heat treatments for SX alloys is developed that involves a heat treatment step at a temperature above the solidus. The super-solidus step gives rise to refined interdendritic microstructure, which is ideal for designing efficient homogenization-solution heat treatment without altering the single crystal microstructure of the specimens.

7. Bridgman Furnace Super-Solidus Processing

7.1 Introduction

In the previous chapter a new concept of a homogenization-solution heat treatment involving a super-solidus step was introduced. It should be noted that those experiments were performed on specimens of simple geometry, and a few millimeters size. In addition, the specimens were cooled quickly from the super-solidus temperature resulting in a highly refined microstructure which is ideal for a short homogenize-solution heat treatment. To investigate the practicality of utilizing the benefits of a super-solidus step on larger components this chapter summarizes the results of the experiments described in Table 4.7 and Figure 4.19, that include a modification to the conventional Bridgman method.

The mould withdrawal rate following super-solidus step is an important variable in Bridgman super-solidus processing as it controls the specimen cooling rate. From an application perspective, it is important to study the effects of withdrawal rates and super-solidus temperature separately. However, to minimize the number of experiments, withdrawal rates and super-solidus temperatures were changed in experiments BS1 to BS5. The microstructure, microporosity, eutectic phase fraction and EPMA of super-solidus processed material are compared with conventionally processed single crystal specimens. Further, the potential advantage of the super-

solidus process is illustrated by examining the solution heat treatment response of Bridgman super-solidus processed specimens described in Table 4.8.

Figure 4.9 illustrates the arrangement of heating elements in the Bridgman furnace chamber. This arrangement is designed for an efficient radiation heat transfer from the concave surfaces of the heating elements to the mould. The furnace control thermocouple, which is situated between two adjacent heating elements, registers a lower temperature than the actual mould/metal temperature. Hence, it became necessary to establish a correlation between the alloy temperature and the furnace temperature during the super-solidus step. To establish such a relationship, microstructures in Figure 6.2 were used as templates and compared with the middle section microstructures of the Bridgman super-solidus processed bars.

7.2 Microstructural Analysis

Figure 7.1 illustrates the microstructural results of experiment BS1 from Table 4. The differences in the transverse section microstructures indicate that there is a temperature gradient along the axis of the bar. However, it is very clear from the alignment of the dendrites that the SX structure of the bar is intact. Further, microstructural features in the middle section of the bar shown in Figure 7.1 compare with Figure 6.2c indicating that the bar was exposed to a super-solidus temperature of about 1330 °C. As the microstructural features in top and bottom sections do not compare with any of the microstructures in Figure 6.2, the temperature variation along the bar is most likely within 10 °C.

Middle sections of SX bars from experiments, BS1, BS2, BS4, and BS5 are shown in Figure 7.2. In general, Figures 7.2a, 7.2b, 7.2c and 7.2d compare with Figures 6.2c, 6.2d, 6.2e and 6.2f respectively. This indicates that the super-solidus temperatures in BS1, BS2, BS4 and BS5 were 1330, 1340, 1350 and 1360 °C respectively. This establishes a correlation between the furnace temperature and the alloy temperature during the Bridgman super-solidus step as shown in Table 7.1 and Figure 7.3.

As shown in Figure 7.4, the specimen resolidified from the super-solidus temperature 1345 °C (BS3) appears unique. This microstructure is quite refined with a significant reduction in eutectic fraction as compared to the highly segregated microstructure of conventionally processed SX specimen. The phase fraction measurement from image analysis revealed 4% eutectic phase fraction in this specimen against 7% in regularly solidified specimen. With a refined microstructure and no defect formation such as blow holes and pipe, the specimen appears to have attained the optimum super-solidus temperature and withdrawal rate.

7.3 Microporosity Analysis

It was observed that very high withdrawal rates as in BS1 and BS5 cause blow holes and pipes in the bars. A moderate withdrawal rate of 200 cm/h was found appropriate producing no blow holes or pipe formation in the specimens (BS3 and BS4) as shown schematically in Figure 7.5. The microporosity levels of Bridgman super-solidus processed specimen (BS3) and regularly solidified SX specimen are compared in Figure 7.6. It is very clear that the Bridgman-resolidified specimen shows

significantly reduced microporosity. Considering that the micropores form only in the interdendritic regions, it is likely that the large micropores in the regularly solidified structure healed during re-solidification following super-solidus step. This lower porosity should contribute to improved mechanical properties of super-solidus processed material

7.4 EPMA

The complete EPMA data is provided in Appendix-A. A comparison of EPMA profiles of regularly solidified and Bridgman super-solidus processed (BS3) specimen is shown in Figure 7.7 for elements which show strong segregation behaviour (Ti, Ta, Cr and Re). The elemental concentration profiles are marginally flatter as they show a slight reduction in the difference between the maximum and minimum points. Also, the undulated profiles of regularly solidified structure are smoothened in the super-solidus processed specimen. This indicates that the resolidified specimen is more homogenous than the regularly solidified specimen. This implies that the super-solidus processing does not change the segregation behaviour of regular SX processing. However, the smoothening of the curves within the dendrite region indicates that super-solidus step gives a quick high temperature homogenization treatment to the regularly solidified structure.

7.5 Stepwise Heat Treatment for Bridgman-Resolidified Specimen

The microstructural results of the stepwise heat treatment on Bridgman resolidified specimen described in Table 4.8 are shown in Figure 7.8 in comparison with the

results obtained for a stepwise heat treatment sequence (SW6, Table 4.3) on conventionally cast specimen. Eutectic phase fractions after solution heat treatments in these specimens were found to be 1.26% and 1.21% respectively. The comparable eutectic phase fractions after solution heat treatment in conventionally processed and re-solidified specimens indicate that there is a significant reduction in the solutioning time for super-solidus processed specimen.

7.6 Conclusions

- A modification to the Bridgman method has been suggested after demonstrating the applicability and advantages of the super-solidus processing of SX superalloys.
- Lower eutectic phase fraction and porosity levels clearly demonstrate the advantages of the modified process.
- As compared to the conventional SX processing for heavily alloyed SX superalloys, a new method involving re-solidification processing of single crystal alloys followed by a shorter solution heat treatment is proposed as shown schematically in Figure 7.9.

8. Thesis Summary and Conclusions

Sub-solidus and super-solidus heat treatments on an experimental single crystal superalloy were investigated over a wide temperature range using DSC, metallography, phase fraction analysis, and EPMA. The most significant contributions of this research work include the development of two new thermal processing methodologies for improving the homogeneity and microstructural control in advanced SX superalloys. Conventional thermal processing methods possess limitations and are expensive for the newer, higher refractory element containing SX alloys, resulting in partially heat treated turbine blade and guide vane components with insufficient long term thermal stability.

In short, the first new homogenizing heat treatment utilizes controlled, continuous heating between the precipitate solvus and the solidus temperatures, rather than the slower and more costly step-wise heat treatment approach used commercially by material vendors. Potential benefits include a more homogenous alloy microstructure with improved thermal stability, as well as a systematic methodology that may be adapted to develop similar new heat treatment procedures for any 3rd or 4th generation SX alloy. The second thermal processing methodology involves a completely new concept of homogenizing the alloy during the Bridgman casting process. Conventional methods restrict heat treatments to sub-solidus temperatures due to negative incipient melting effects. The newly investigated methodology involves applying the super-solidus heat treatment immediately after casting directly in the

Bridgman furnace. Results of this thesis show that although the solidus temperature is the upper limit for conventional stepwise homogenization heat treatments, a controlled super-solidus exposure gives rise to significant microstructural refinement including lower casting porosity without adversely affecting the SX structure of the alloy. This new methodology has a significant potential for the current and the next generation of SX alloys that possess highly segregated cast microstructures due to high refractory element contents. By utilizing this method, a more refined as-solidified microstructure can be achieved and homogenization-solution heat treatment becomes easier and less expensive.

8.1 Conclusions:

1. The rigorous study of conventional stepwise heat treatments during the course of this thesis revealed that sub-solvus heat treatment holding steps stabilize the eutectic phase, while super-solvus heat treatment steps effectively solutionize eutectic γ' phase. However, irrespective of the temperature or duration of the lower temperature hold time steps, extended holding at and above the solidus temperature causes incipient melting due to *up-hill diffusion* in the interdendritic regions. Based on results of the stepwise heat treatments in this study, a continuous heating procedure, between the solvus and the solidus temperatures, has been proposed that effectively homogenizes and solutions the heavily alloyed SX superalloys without causing incipient melting

2. Epitaxial growth of fine resolidification dendrites occurs during super-solidus exposure heat treatments followed by quick cooling. Though the solidus temperature is the upper limit for conventional stepwise homogenization-solution heat treatments, the results of super-solidus heat treatments indicate that a controlled super-solidus exposure gives rise to significant microstructural refinement without affecting the SX microstructure, thus making it possible to use the shorter homogenization-solution heat treatments.
3. This thesis introduces the concept of super-solidus heat treatment that is implemented as an integral part of the Bridgman SX casting process. The potential advantages of this modified method are illustrated by performing solution heat treatments on both super-solidus and normally processed specimens. To obtain a more refined microstructure with lower microporosity level a modification to Bridgman SX processing involving a well defined and calibrated *super-solidus* heat treatment step is proposed.

8.2 Future Work

1. This thesis provides experimental evidence for “up-hill diffusion” during extended holding above the solvus temperature causing incipient melting in the interdendritic regions. However, the actual mechanism of up-hill diffusion in a multicomponent system like a SX superalloy is not well understood. More research is needed possibly, using thermodynamic kinetic modelling coupled

with experiments and characterization to develop a mathematical model for this mechanism.

2. The continuous heating homogenization-solution heat treatments proposed in this thesis are based on the heat treatment response of an experimental SX alloy. However, it is important to determine if the proposed procedure can be implemented on commercial SX alloys such as CMSX-10, PWA-1484.
3. The advantages of super-solidus exposure in controlling the microstructure of SX alloys have been confirmed in this thesis. However, the Bridgman super-solidus processing should be further optimized. It is suggested that heat transfer modelling for the super-solidus step be undertaken to obtain the optimal holding time and withdrawal rate. A faster cooling of the mould by argon jet impingement or liquid metal cooling (LMC) during the super-solidus withdrawal in the cold chamber of the Bridgman furnace could be implemented to obtain even more refined re-solidified microstructure.
4. The reduced microporosity in the super-solidus processed SX bars is clearly demonstrated in this work. However, it is important to confirm the improvement in properties by performing mechanical tests including creep and fatigue tests, and compare with the properties of regularly processed SX bars. Once reduced processing time and improved properties are confirmed,

through qualification testing then there would be sufficient justification to implement the super-solidus processing on actual SX turbine parts.

5. As controlled super-solidus heat treatment retains the SX structure due to epitaxial growth during re-solidification and this advantage or feature can be implemented in joining and repair techniques for DS and SX superalloys. Unlike transient liquid phase bonding (TLP) method, super-solidus joining technique does not require addition of a melting point depressant and hence, it is more likely that the resulting joint would be more stable. It is worth performing super-solidus joining experiments on SX and DS alloys followed by heat treatments and mechanical testing.

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Table 2.1: Effects of alloying elements in Ni-base superalloys [26].

Element	Matrix Strengthening	Increase in γ' volume fraction	Other Effects
Cr	moderate	moderate	improves corrosion resistance promotes TCP phases
Mo	high	moderate	increases density
W	high	moderate	promotes TCP phases
Ta	high	large	raises solidus temperature
Nb	high	large	promotes γ' and δ phases
Ti	moderate	very large	lowers density
Al	moderate	very large	improves oxidation resistance
Co	slight	moderate	raises solidus
Re	moderate		retards γ' coarsening increases misfit
Ru	moderate		stabilizes microstructure retards TCP phase formation

Table 2.2: Compositions of few commercial single crystal (SX) superalloys.

	Cr	Co	Mo	W	Ta	Nb	Al	Ti	Hf	Re	Ru	Ni
1st Generation												
PWA1480	10	5	0	4	12		5	1.5				Bal
Rene N4	9	8	2	6	4	0.5	3.7	4.2				Bal
SRR99	8	5	0	10	3		5.5	2.2				Bal
CMSX2	8	5	0.6	8	6		5.6	1				Bal
CMSX6	10	5	3	0	2		4.8	4.7	0.1			Bal
									0			Bal
2nd Generation												
PWA1484	5	10	2	6	9		5.6	0	0.1	3		Bal
Rene N5	7	8	2	5	7		6.2	0	0.2	3		Bal
CMSX4	7	9	0.6	6	7		5.6	1	0.1	3		Bal
3rd Generation												
Rene N6	4.2	12.5	1.4	6	7.2	0.1	5.75	0	0.15	5.4		Bal
CMSX10	2	3	0.4	5	8		5.7	0.2	0.03	6		Bal
TMS75	3	12	2	6	6		6	0	0.1	5		Bal
4th Generation												
MC-NG	4	0.2	1	5	5		6	0.5	0.1	4	4	Bal
EPM-102	2.0	16.5	2.0	6.0	8.25		5.55		0.15	5.95	3	Bal
TMS-138	2.9	5.9	2.9	5.9	5.6		5.9		0.1	4.9	2	
Next Generation												
TMS-162	2.9	5.8	3.9	5.8	5.6		5.8		0.09	4.9	6	Bal
TMS-172	2.8	5.6	2.8	5.6	5.6		5.6		0.1	6.9	5	Bal

Table 3.1: Standard heat treatment procedure for the third generation single crystal superalloy, CMSX-10 [51].

Solutionizing	1315 °C/1h + 1329 °C/2h + 1335 °C/2h + 1340 °C/2h + 1346 °C/2h + 1352 °C/3h + 1357 °C/3h + 1360 °C/3h + 1363 °C/10h + 1365°C/15h + Helium Quench
Aging	1150 °C/4h/Air cool + 870 °C/24h/Air cool + 760 °C/30h + Air Cool

Table 4.1 Nominal compositions of indigenously designed experimental alloys [26].

Alloy	Chemical composition* (wt. %)					Total refractory (wt. %)	Alloy density (g/cm ³)
	Ni	Ta	W	Re	Ru	W+Ta+Co+Re+Ru	
Alloy A	63.5	12	3	1	0	21	9.77
Alloy B	63.5	12	2	2	0	21	9.78
Alloy C	63.5	12	1	3	0	21	9.80
Alloy D	63.5	12	0	4	0	21	9.81
Alloy E	60.5	12	4	3	0	24	10.11
Alloy F	60.5	11	1	3	4	24	9.85
* In addition, each alloy also contains: 7.5%Cr + 5%Co + 2%Mo + 1%Ti + 5%Al.							

Table 4.2: Comparison of compositions of the experimental alloy (Alloy-B) and the commercial alloy, PWA 1484[26].

Alloy	Ta	W	Re	Co	Mo	Cr	Ti	Al	Ni
Alloy-B (nominal composition)	12	2	2	5	2	7.5	1	5	Balance
Alloy-B (wet chemical analysis)	12.04	2.05	2.07	5.16	1.9	7.49	1.01	4.75	Balance
PWA 1484 (Nominal composition)	9	6	3	10	2	5	-	5.6	Balance

Table 4.3: Stepwise homogenization-solution heat treatments.

Expt. No.	Heat Treatment
SW1	1170 °C/15h + 1250 °C/2h + 1280 °C/2h + 1300 °C/2h + 1310 °C/2h
SW2	1170 °C/15h + 1250 °C/2h + 1280 °C/5h + 1300 °C/2h + 1310 °C/2h + 1315 °C/2h + 1320 °C/2h + 1325 °C/2h
SW3	1170 °C/2h + 1250 °C/2h + 1280 °C/15h + 1300 °C/2h + 1310 °C/2h + 1320 °C/2h
SW4	1170 °C/2h + 1250 °C/2h + 1280 °C/5h + 1300 °C/2h + 1310 °C/5h + 1315 °C/15h
SW5	1170 °C/2h + 1250 °C/2h + 1280 °C/5h + 1300 °C/5h + 1310 °C/5h, 10h, 15h
SW6	1280 °C/2h + 1295 °C/2h + 1305 °C/2h, 10h, 20h

Table 4.4: Continuous heating homogenization-solution heat treatments.

Expt. No.	Heat Treatment	Heating Rate (°C /h)
CH1	1285 °C → 1310 °C	1
CH2	1285 °C → 1305 °C	1
CH3	1285 °C → 1305 °C	0.5
CH4	1295 °C → 1305 °C	0.25

Table 4.5: Short exposure heat treatments.

Experiment No.	SE1	SE2	SE3	SE4	SE5	SE6	SE7	SE8	SE9
Temp (°C)	1250	1300	1310	1320	1330	1340	1350	1360	1345
Exposure (h)	2	2	2	2	2	2	2	2	0.5
Cooling Method	Water quench								Air cool

Table 4.6: Super-solidus homogenization-solution heat treatment.

1350 °C/1 h/WQ + 1250 °C/2 h/WQ + 1300 °C/2 h/WQ + 1310 °C/2 h/WQ + 1320 °C/2 h/WQ

Table 4.7: Bridgman super-solidus processing.

Expt. No.	Standard Bridgman Process		Super-Solidus Step	
	Temperature (°C)	Withdrawal Rate (cm/h)	Temperature (°C)	Withdrawal Rate (cm/h)
BS1	1585	20	1330	2400
BS2	1585	20	1340	No withdrawal
BS3	1585	20	1345	200
BS4	1585	20	1350	200
BS5	1585	20	1360	1200

Table 4.8: Stepwise homogenization-solution heat treatment for Bridgman super-solidus processed specimen (BS3).

BS3+1290 °C/2h/WQ + 1300 °C/2h/WQ + 1305 °C/2h/WQ

Table 5.1: Eutectic Phase Fraction Analysis.

Expt. No	Heat Treatment Step	Eutectic Phase Fraction (%)
-	Solidified	6.99
SW1	1170°C/15h + 1250°C/2h + 1280°C/2h	3.29
SW2	1170°C/15h + 1250°C/2h + 1280°C/5h	3.38
SW3	1170°C/2h + 1250°C/2h + 1280°C/15h	4.23
SW6	1280°C/2h	4.76
	1280°C/2h + 1295°C/2h	3.78
	1280°C/2h + 1295°C/2h + 1305°C/2h	2.33
	1280°C/2h + 1295°C/2h + 1305°C/10h	1.26
	1280°C/2h + 1295°C/2h + 1305°C/20h	0.91

Table 5.2: Variation of homogenization with heat treatment.

Element	Profile Statistics	Concentration (wt %)				
		Solidified	SW6			
			1295°C /2h	1305°C /2h	1305°C /10h	1305°C /20h
Al	max	6.13	5.969	5.545	5.98	6.414
	min	4.55	4.668	4.715	4.774	4.711
	Diff	1.58	1.301	0.83	1.206	1.703
Cr	max	8.20	8.067	7.685	7.886	7.695
	min	2.77	3.975	4.651	4.653	2.716
	Diff	5.43	4.092	3.034	3.233	4.979
Ni	max	66.05	65.343	64.492	65.401	67.35
	min	61.87	61.626	61.963	63.155	62.948
	Diff	4.17	3.717	2.529	2.246	4.402
Co	max	5.17	5.261	5.074	5.201	5.216
	min	3.65	4.044	4.27	4.252	3.724
	Diff	1.52	1.217	0.804	0.949	1.492
Ti	max	1.65	1.228	1.229	1.225	1.347
	min	0.66	0.922	0.999	0.977	1.001
	Diff	0.99	0.306	0.23	0.248	0.346
Re	max	2.80	2.6	2.148	2.386	2.261
	min	0.29	0.735	0.946	0.928	0.316
	Diff	2.51	1.865	1.202	1.458	1.945
Ta	max	18.21	15.411	14.457	15.252	17.104
	min	9.41	10.885	11.913	11.89	11.967
	Diff	8.81	4.526	2.544	3.362	5.137
Mo	max	2.08	1.967	1.894	1.881	1.947
	min	0.50	0.878	1.28	0.978	0.399
	Diff	1.58	1.089	0.614	0.903	1.548
W	max	2.83	2.678	2.102	2.263	2.195
	min	0.63	1.313	1.221	1.233	0.82
	Diff	2.20	1.365	0.881	1.03	1.375

Table 5.3: Results of continuous heating experiments.

Expt No.	Experiment	Heating Rate (°C/h)	Result	Residual Eutectic (%)
CH1	1285°C → 1310°C	1	Incipient melting	-
CH2	1285°C → 1305°C	1	No incipient melting	1.7
CH3	1285°C → 1305°C	0.5	No incipient melting	1.4
CH4	1295°C → 1305°C	0.25	No incipient melting	0.5

Table 7.1: Temperature correlation for Bridgman super-solidus step.

Experiment No.	Super-solidus step	
	Furnace temperature (°C)	Alloy temperature (°C)
BS1	1285	1330
BS2	1291	1340
BS4	1296	1350
BS5	1301	1360

Figure 1.1: Turbine entry temperature (TET) versus year of entry to service showing major technical advances and Rolls-Royce engines [6].

Figure 1.2: A schematic illustration of constraints limiting the design space available for future superalloys [6].

Figure 2.1: A schematic of cast turbine blades showing the grain structures of: a) conventionally cast, b) directionally solidified, and c) single crystal turbine blades (adopted from reference [18]).

Figure 2.2: Comparison of creep behaviour of the superalloy MAR-M200 in the conventionally cast, the directionally solidified, and the single crystal form [13].

Figure 2.5: Scanning Electron Micrograph of a heat treated and unetched SX superalloy showing the uniformly distributed γ' precipitates (grey region) within the matrix of γ phase (bright region) [58].

Figure 2.6: Scanning Electron Micrograph of a heat treated and etched SX superalloy showing the cuboids of γ' and channels of γ phase partly dissolved by etching [9].

Figure 2.7: Creep life versus volume fraction of γ' in SX superalloys [18].

Figure 2.8: A schematic of crystal structures showing: a) ordered $L1_2$ structure of γ' and b) disordered FCC structure of γ phase [6].

Figure 2.9: Transmission electron microscope bright field image of a SX superalloy showing the dislocations being hindered by the γ' cuboids aligned along $\langle 001 \rangle$ [58].

Figure 2.10: Selected Area Diffraction pattern corresponding to Figure 2.9 showing the regular FCC pattern from γ phase with superimposed superlattice reflections from coherent γ' phase [58].

Figure 2.11: Evolution of the composition of Ni-base superalloys over 50 years [6].

Figure 2.12: Schematic of an industrial Bridgman furnace [6].

Figure 2.13: Schematic of thermal zones and heat flow in a Bridgman furnace [27].

Figure 2.14: Schematic of the Bridgman method of producing DS turbine blades [15].

Figure 2.15: A schematic of competitive columnar growths forming a crystallographic texture along $\langle 001 \rangle$ (adopted from reference [30]).

Figure 2.16: Crystallographic pole figures of a DS casting at different heights from the chill platen showing a strong $\langle 001 \rangle$ texture formation [12].

Figure 2.17: Schematic showing: a) Bridgman SX casting with grain selector geometry in a shell mould, b) grain selector spiral at the bottom of as-cast turbine blade[26].

Figure 2.18: Schematic showing: (a) simulation of solidification in a double spiral grain selector geometry, (b₁-e₁) variation of pole figures along spiral height, and (b₂-e₂) histogram of grain orientations at locations b to e in (a) [26].

Figure 2.19: A schematic of shell mould assembly with a single crystal seed [59].

Figure 2.20: Schematic of temperature gradient during directional solidification [19].

Figure 2.21: A schematic of the superalloy composition superimposed on binary Ni-Al phase diagram.

Figure 2.22: A schematic of planar front solidification sequence of an alloy [29].

Figure 2.23: Schematic of cellular solidification with intercellular eutectic [29].

2.24: Schematic showing effect of increasing growth kinetics on the solidification morphology; plane front solidification converting to cellular growth which leads to dendritic growth along [001] [51].

Figure 3.1: Comparison of transverse sections of: (a) solidified single crystal superalloy showing properly aligned dendrites, (b) directionally solidified superalloys showing two misaligned grains forming a grain boundary [55].

Figure 3.2: Unetched transverse section of a single crystal superalloy showing $\langle 001 \rangle$ aligned dendritic microstructure with micropores seen as bright spots at the interdendritic region [9].

Figure 3.3: Optical micrograph of a solidified and etched single crystal superalloy showing a highly segregated structure and the presence of the interdendritic eutectic phase [9].

Figure 3.4: EPMA composition maps of: a) Re, b) Ta, c) Ti, and d) W, illustrating microsegregation in solidified superalloy [54].

Figure 3.5: EPMA profile of a superalloy showing the segregation across the dendrite core and interdendritic (ID) eutectic region [9].

Figure 3.6: Solidified microstructures illustrating the distribution of size and morphology of γ precipitates at the dendrite core and the interdendritic region [9].

Figure 3.7: A high magnification microstructure showing the morphology of eutectic phase [9].

Figure 4.1: DSC plots of experimental superalloys A-F; Alloy B is designated as 2.1 [9].

Figure 4.2: As-received master alloy bars.

Figure 4.3: Image of experimental material and consumables; 1) molybdenum wires, 2) molybdenum foil, 3) alumina spacer, 4) seed crystal, 5) rough ground master alloy, 6) alumina mould, and 7) a prepared mould assembly ready for Bridgman processing.

Figure 4.4: Carleton University DS furnace [9].

Figure 4.5: Schematic of Bridgman SX-facility [courtesy, H. Saari].

Figure 4.6: An image showing the copper chill platen in the cold chamber.

Figure 4.7: An image showing the loaded mould assembly in the cold chamber.

Figure 4.8: Temperature profile of Bridgman hot chamber showing the time zones of activity in the furnace as follows:

- 1) mould raised to hot chamber and heated under high vacuum,**
- 2) furnace chamber back-filled with argon and held at 1585 °C,**
- 3) mould withdrawn to cold chamber at 20 cm/h, and**
- 4) furnace cooled to ambient temperature.**

Figure 4.9: Schematic of transverse section of Bridgman furnace showing the position of temperature control thermocouple.

Figure 4.10: Schematic showing the conditions within the mould just before withdrawal and temperature gradient (G_L) within the alloy as measured at the liquidus temperature (T_L) [9].

Figure 4.11: Schematic of the possible heat transfer modes during DS/SX casting [8].

Figure 4.13: Image showing Bridgman processed SX bar after the mould is broken.

Figure 4.14: The bar on the left shows blowholes due to argon-backfill before melting the alloy, the bar at the centre shows patchy surface due to the dirt picked-up from the chill plate, the bar on the right produced using the improved process developed as part of this thesis showing a clean surface finish.

Figure 4.15: The SX bar on left showing the patchy surface due to the alloy melt-back region picking up dirt from the chill plate. The bar on right showing the alloy melt down not reaching the ceramic separator/chill plate and hence giving rise to a clean surface.

Figure 4.16: Schematic showing the theme of stepwise heat treatment (Table 4.3) to study the effect of extended holding at various temperatures.

Figure 4.17: Schematic showing the programmed temperature profile of continuously heating experiments (Table 4.4) at different heating rates.

Figure 4.18: Schematic showing the theme of the super-solidus heat treatment (Table 4.6).

Figure 4.19: Programmed hot chamber temperature profile for super-solidus processing in Bridgman furnace showing the time zones of activity as follows:

- 1) mould raised to hot chamber and heated under high vacuum,**
- 2) back-filled with argon and held at a superheat temperature,**
- 3) mould withdrawn to cold chamber at 20 cm/h,**
- 4) mould at cold chamber, while furnace cooled to a super-solidus temperature,**
- 5) mould raised to hot chamber and held at the super-solidus temperature for 30 min,**
- 6) mould withdrawn rapidly, and**
- 7) furnace cooled to ambient temperature.**

Figure 4.20: A sample of furnace recorded chart showing an additional holding step for the super-solidus withdrawal.

Figure 5.1: Transverse microstructures of solidified SX alloy:
a) showing highly segregated dendritic structure indicating the crystallographic directions of primary and secondary dendrite arms and primary dendrite arm spacing (PDAS), and b) showing fine γ' precipitates within the dendrite and coarse cellular γ - γ' eutectic at the interdendritic (ID) region.

Figure 5.2: Results of the stepwise experiment SW1 showing the microstructural development after:

- a) 1170 °C/15 h step showing no visible change in the microstructure,**
- b) 1250 °C/2 h step showing denuded region around the eutectic,**
- c) 1280 °C/2 h step showing start of solutionizing at dendrite cores,**
- d) 1300 °C/2 h showing the residual eutectic and fully solutionized dendrites, and**
- e) 1310 °C/2 h indicating onset of incipient melting at the interdendritic region.**

Figure 5.3: Results of the experiment, SW2 showing the microstructural development after:

- a) 1310 °C/2 h showing no sign of incipient melting,**
- b) 1315 °C/2h showing significantly reduced eutectic phase fraction,**
- c) 1320 °C/2 h showing a sudden occurrence of incipient melting, and**
- d) 1325 °C/2h confirming incipient melting within core as well as interdendritic regions.**

Figure 5.4: Microstructural development in the experiment SW3 after:
a) 1170 °C/2 h, b) 1250 °C/2 h, c) 1280 °C /15 h, d) 1300 °C/2 h, e) 1310 °C/2 h,
and f) 1320 °C/2 h.

Figure 5.5: Comparison of microstructures indicating the stabilization of eutectic as an effect of extended holding at 1280 °C in: a) SW1, b) SW2, and c) SW3.

Figure 5.6: Comparison of high magnification microstructures in SW3: a) before, and b) after 1320 °C/2 h step indicating formation of cellular colonies and hence the occurrence of eutectic reaction at 1320 °C

Figure 5.7: Microstructure at the end of SW4 showing incipient melting after holding at 1315 °C for 15 h.

Figure 5.8: Microstructural change of the alloy in the experiment SW5 after: a) 1300 °C/5 h, b) 1310 °C/5 h, c) 1310 °C/10 h, and d) 1310 °C/15 h steps showing a systematic progression of incipient melting with extended holding.

Figure 5.9: Microstructural change of the alloy in the experiment SW6 after: a)1295 °C/2 h, b)1305 °C/2 h, c)1305 °C/10 h, d)1305 °C/20 h showing a systematic reduction of eutectic phase.

Figure 5.10 Incipient melting map of the alloy.

Figure 5.11: A comparison of variation of eutectic fraction with:
a) holding time at 1280 °C from experiments SW1, SW2, and SW3,
b) holding time at 1305 °C from experiments SW6,
c) holding temperature from experiment SW6.

Figure 5.12: An illustration of EPMA composition measurements.

Figure 5.13: Composition profile from eutectic to core region showing increased homogenization with increased holding temperature.

Figure 5.14: Isothermal composition profiles from eutectic to core region showing a reduction in homogenization with extended holding at 1305 °C.

Figure 5.15: Comparison of macrostructures after the continuous heating experiments: a) CH1, b) CH2, c) CH3, and d) CH4 from Table 4.4.

Figure 5.16: Comparison of: a) conventional step-wise homogenization-solution heat treatment method, and b) proposed continuous heating homogenization-solution heat treatment scheme.

**Figure 6.1: Microstructures after short exposure heat treatments:
a) SE1 exposed to 1250 °C, and b) SE2 exposed to 1300 °C for 2hr.**

Figure 6.2: Microstructures after holding at: a) 1310 °C, b) 1320 °C, c) 1330 °C, d) 1340 °C, e) 1350 °C, and f) 1360 °C for 2hr

Figure 6.3 Comparison of microstructures of the alloy: a) solidified condition, b) 1340 °C for 2 h followed by water quenching (SE6), c) 1350 °C for 2 h followed by water quenching (SE7), and d) 1345 °C for 0.5 h followed by air cooling (SE9).

Figure 6.4: Comparison of: a) regularly solidified SX structure, and b) SX structure quenched from 1350 °C showing refinement of interdendritic eutectic.

Figure 6.5: Microstructural response of the super-solidus homogenization-solution heat treatment from Table 4.6 after: a)1350 °C , b)1250 °C, c) 1300 °C, d) 1310°C, and e)1320 °C steps.

Figure 6.6: High magnification microstructures showing microstructural modifications at the interdendritic regions during super-solidus homogenization-solution heat treatment after: a) 1350 °C, b) 1250 °C c) 1300 °C, d) 1310 °C, and e) 1320 °C steps.

Figure 6.7: Comparison of: a) interdendritic region of SX after super-solidus heat treatment showing the absence of grain boundaries and presence of undissolved discrete sections of γ' within a continuous matrix, b) a polycrystalline superalloy after homogenization-solution heat treatment showing grain boundaries [57].

Figure 7.1: Schematic of super-solidus processed superalloy bar showing microstructural variation at bottom, middle and top transverse sections.

Figure 7.2: Middle section microstructures of Bridgman super-solidus processed SX bars: a) BS1, b) BS2, c) BS4, and d) BS5.

Figure 7.3: Correlation between the furnace temperature and alloy temperature during super-solidus step in Bridgman furnace.

Figure 7.4: Comparison of microstructures of SX bars:
a) conventionally solidified specimen showing a highly segregated structure, and
b) super-solidus processed specimen (BS3) showing a refined microstructure
with a significantly reduced eutectic fraction.

Figure 7.5: Schematic of super-solidus processed superalloy bars showing:
a) pipe formation in rapidly withdrawn bar (experiments BS1 and BS5),
b) good quality bar withdrawn at a moderate speed (experiments BS3, BS4).

**7.6: Comparison of microstructures of SX bars before etching:
a) conventionally solidified specimen showing a high level of microporosity, and
b) super-solidus processed specimen (BS3) showing a significantly reduced level
of porosity.**

Figure 7.7: Comparison of EPMA profiles of Ta, Ti, Re and Cr on conventionally solidified specimen and super-solidus processed specimen (BS3).

Figure 7.8: Comparison of microstructures after stepwise heat treatments:
a) after 14 h solution heat treatment on regularly solidified specimen (SW6), and
b) after 6 h solution heat treatment on super-solidus processed specimen
(Table 4.8).

Figure 7.9: Schematic of temperature profiles: a) conventional Bridgman SX-casting followed by multi-step solution heat treatment, b) proposed Bridgman super-solidus process followed by two-step solution heat treatment.

Appendix-A

Spot EPMA data from eutectic (Spot No.1) to dendrite core (Spot No. 5).										
Spot No.	Distance (μm)	Al	Cr	Ni	Co	Ti	Re	Ta	Mo	W
As-solidified condition [adopted from reference 9]										
1	0	5.01	7.32	63.54	4.74	0.99	1.82	12.40	1.69	2.04
2	25	4.74	7.68	63.64	4.96	0.78	2.50	10.60	1.61	2.70
3	50	4.79	7.49	64.32	5.08	0.75	2.69	9.94	1.49	2.97
4	75	4.66	8.17	63.18	5.13	0.83	2.65	10.48	1.74	2.55
5	100	4.31	9.22	60.11	5.10	1.19	2.10	12.79	2.58	1.79
After 1295 °C/2h (SW6)										
1	0	5.969	3.975	65.343	4.044	1.228	0.735	15.411	0.878	1.313
2	25	4.705	7.801	61.626	5.108	0.922	2.193	10.885	1.775	2.36
3	50	4.712	7.965	63.06	5.155	0.948	2.6	10.931	1.967	2.678
4	75	4.721	8.067	62.692	5.261	0.933	2.594	10.909	1.913	2.578
5	100	4.668	7.959	62.413	5.202	0.942	2.53	11.259	1.953	2.508
After 1305 °C/2h (SW6)										
1	0	5.545	4.651	64.492	4.27	1.229	0.946	14.457	1.28	1.221
2	25	4.752	7.685	62.134	5.074	1.001	1.99	11.913	1.894	2.055
3	50	4.811	7.605	62.548	4.994	1.014	2.148	11.984	1.81	2.102
4	75	4.809	7.618	62.801	5.062	1.022	1.73	12.414	1.869	2.069
5	100	4.715	7.574	61.963	5.074	0.999	1.817	12.428	1.877	1.795
After 1305 °C/10h (SW6)										
1	0	5.98	4.653	65.401	4.252	1.225	0.928	15.252	0.978	1.233
2	25	4.821	7.786	63.155	5.125	1.022	1.943	12.274	1.796	2.17
3	50	4.774	7.854	63.201	5.201	0.996	2.107	11.89	1.881	2.203
4	75	4.806	7.886	63.187	5.136	0.977	2.386	11.903	1.863	2.263
5	100	4.818	7.809	63.454	5.135	1.017	2.343	12.059	1.861	2.217
After 1305 °C/20h (SW6)										
1	0	6.414	2.716	67.35	3.724	1.347	0.316	17.104	0.399	0.82
2	25	4.773	7.68	62.948	5.216	1.014	2.15	12.169	1.808	2.067
3	50	4.795	7.66	63.458	5.13	1.016	2.19	12.275	1.855	2.016
4	75	4.711	7.695	63.199	5.16	1.001	2.196	11.967	1.795	2.195
5	100	4.711	7.682	63.206	5.161	1.002	2.261	12.153	1.947	2.091
After 1310 °C/2h (SW1)										
1	0	6.191	4.413	65.807	4.001	1.459	0.711	15.964	0.941	0.932
2	25	5.109	7.48	64.984	4.909	0.996	1.782	12.146	1.759	1.852
3	50	5.102	7.82	64.494	5.031	1.011	1.965	11.619	1.884	2.056
4	75	4.963	7.818	63.707	5.02	0.998	2.259	11.623	1.955	2.283
5	100	4.932	7.999	63.772	5.081	1.002	2.422	11.464	1.788	2.3
Bridgman Super-Solidus processed (BS3)										
1	0	6.123	3.297	65.897	3.858	1.525	0.442	17.15	0.698	0.857
2	25	4.637	7.96	63.581	5.15	1.117	1.911	12.057	2.08	1.835
3	50	5.003	7.723	65.025	5.202	0.834	2.477	10.726	1.776	2.526
4	75	5.01	7.668	64.188	5.315	0.765	2.728	9.783	1.692	2.754
5	100	4.93	7.698	64.761	5.208	0.815	2.612	9.98	1.76	2.624

Appendix-B

1-sigma error corresponding to EPMA data in Appendix-A.

Spot No.	Distance (μm)	Al	Cr	Ni	Co	Ti	Re	Ta	Mo	W
As-solidified condition										
1	0	0.035	0.051	0.445	0.038	0.01	0.036	0.112	0.047	0.039
2	25	0.033	0.054	0.445	0.04	0.01	0.045	0.106	0.047	0.046
3	50	0.034	0.052	0.45	0.04	0.01	0.048	0.099	0.045	0.05
4	75	0.033	0.057	0.442	0.041	0.01	0.048	0.105	0.049	0.046
5	100	0.03	0.065	0.421	0.041	0.013	0.04	0.115	0.062	0.036
After 1295 °C/2h (SW6)										
1	0	0.042	0.032	0.45	0.04	0.014	0.071	0.172	0.045	0.074
2	25	0.032	0.056	0.431	0.047	0.013	0.084	0.135	0.059	0.084
3	50	0.033	0.056	0.433	0.047	0.012	0.084	0.139	0.059	0.082
4	75	0.033	0.055	0.435	0.047	0.012	0.086	0.131	0.057	0.084
5	100	0.033	0.055	0.433	0.046	0.012	0.084	0.132	0.057	0.08
After 1305 °C/2h (SW6)										
1	0	0.039	0.033	0.451	0.043	0.014	0.077	0.159	0.052	0.078
2	25	0.033	0.054	0.435	0.046	0.013	0.084	0.143	0.061	0.082
3	50	0.034	0.053	0.438	0.045	0.012	0.086	0.144	0.06	0.082
4	75	0.034	0.053	0.44	0.046	0.012	0.083	0.149	0.06	0.081
5	100	0.033	0.053	0.434	0.046	0.013	0.084	0.149	0.06	0.079
After 1305 °C/10h (SW6)										
1	0	0.042	0.032	0.458	0.038	0.013	0.071	0.168	0.047	0.073
2	25	0.034	0.055	0.442	0.046	0.012	0.082	0.147	0.057	0.078
3	50	0.033	0.055	0.442	0.047	0.012	0.082	0.143	0.058	0.079
4	75	0.034	0.055	0.442	0.046	0.012	0.084	0.143	0.058	0.081
5	100	0.034	0.055	0.444	0.046	0.012	0.084	0.145	0.058	0.08
After 1305 °C/20h (SW6)										
1	0	0.045	0.022	0.471	0.037	0.013	0.066	0.171	0.038	0.07
2	25	0.033	0.054	0.44	0.047	0.012	0.08	0.146	0.056	0.076
3	50	0.034	0.054	0.444	0.046	0.012	0.083	0.147	0.058	0.077
4	75	0.033	0.054	0.442	0.046	0.012	0.081	0.144	0.057	0.079
5	100	0.033	0.053	0.442	0.046	0.012	0.084	0.146	0.058	0.079
After 1310 °C/2h (SW1)										
1	0	0.043	0.035	0.46	0.04	0.014	0.074	0.175	0.048	0.074
2	25	0.036	0.052	0.455	0.044	0.013	0.084	0.146	0.06	0.079
3	50	0.036	0.055	0.451	0.045	0.012	0.086	0.139	0.06	0.084
4	75	0.035	0.055	0.444	0.045	0.013	0.088	0.139	0.06	0.084
5	100	0.034	0.056	0.446	0.046	0.013	0.089	0.138	0.059	0.083
Super-solidus processed (BS3)										
1	0	0.043	0.026	0.461	0.039	0.015	0.066	0.172	0.041	0.067
2	25	0.032	0.056	0.445	0.046	0.012	0.078	0.133	0.058	0.075
3	50	0.035	0.054	0.455	0.047	0.011	0.082	0.129	0.055	0.078
4	75	0.035	0.054	0.449	0.048	0.011	0.085	0.127	0.054	0.08
5	100	0.034	0.054	0.453	0.047	0.01	0.086	0.13	0.054	0.081