STUDY OF BACK-DIFFUSION IN THE NICKEL-BASE SINGLE CRYSTAL SUPERALLOY RR-2100

by

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Abstract

Nickel–base superalloys have been an topic of active research for over five decades and the findings from various researchers worldwide have had a direct impact not only on different areas of materials science but also on applications thereof, in particular the aircraft industry, i.e. the aeroengine. One of the primary concerns of aircraft engine manufacturers has been the problem of microsegregation in turbine blade alloys. This phenomenon which is present in almost all cast products occurs due to the partitioning of solute between the solid and the liquid phases during solidification and is ultimately the source of several types of defects such freckling and white spots in castings resulting in rejection of defective products. Since microsegregation results in a heterogeneous distribution of alloying elements in the cast product it is deleterious to the component’s thermo–mechanical properties as well as to its resistance to environmental attack. Thus, much of the current work in superalloy technology has been directed towards gaining a better understanding of microsegregation in different alloys through experimentation coupled with efforts leading towards finding a means of satisfactorily predicting its effects and also to a degree controlling it.

Over the years efforts have culminated in many models of microsegregation having been developed for different alloy systems with reasonably acceptable predictive capacities. Nearly all of these models consider the phenomenon of back–diffusion in the solid which serves to reduce the degree of microsegregation in the final cast product by redistributing the solute during solidification. In Ni–base superalloys however, evidence for back diffusion is scarce and only a handful of models of microsegregation are available. The work contained in this thesis addresses the issue of obtaining experimental proof for back diffusion in a Ni–base single crystal superalloy.
The study was also aimed at developing a suitable model to predict the microsegregation in the alloy. Directional solidification experiments were conducted in a Directional Solidification and Quench (DSQ) furnace for producing cast single crystal specimens of the alloy RR-2100 which were characterized using Differential Scanning Calorimetry (DSC) for the alloy's solidification behaviour and range. Electron-probe microanalysis (EPMA) experiments were conducted on specimens prepared in this way to obtain compositional data in the mushy zone. The raw data from these experiments were sorted and interpreted with the model of microsegregation. The agreement between the model's predictions and the experimental data were found to be reasonably good. The analysis revealed evidence for back diffusion in RR-2100 nickel-base single crystal superalloy and the measures of the diffusivities of the solutes obtained were found to be consistent with previous findings in the literature.
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<td>Differential Thermal Analysis</td>
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<td>DS</td>
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<td>DSQ</td>
<td>Directional Solidification and Quench</td>
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<td>EPMA</td>
<td>Electron Probe Microanalysis</td>
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<td>VAR</td>
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<td>VIM</td>
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Chapter 1

Introduction
1.1 The Nickel–base Superalloys

The term "superalloy" was coined shortly after the Second World War. At the time, due to rapid advances in technology fueled by the escalating competition between nations, a new group of alloys was developed for use in turbochargers and aircraft engines. The key requirement was performance at elevated temperatures. Since then the range of application of this class of materials has broadened to encompass land based and areoengine gas turbines, rocket engines, power and chemical plants. These alloys have the ability to retain their strength under extreme conditions of pressures, temperatures and environments and perform well even after prolonged exposure. Their versatility is a direct result of careful tailoring of the alloy composition.

The evolution of the aircraft jet engine (itself just about 60 years old) has been defined by the improvement of the temperature capability of materials in terms of their specific strength or toughness and modulus, as well as durability defined by creep and fatigue and resistance to turbine combustion products. The allowable compressor outlet temperature and the turbine entry temperature directly affect the efficiency of the engine, demanding materials to perform at higher and higher temperatures, while density defines the thrust-to-weight ratio and specific fuel consumption. Nickel–base superalloys were found to be well suited for such an application and were introduced as the materials for the turbine section in the 1940's and this set the standard for the development of industry. Titanium was a contemporary to nickel and was first employed as the compressor blade material in the 1950's. Since then the temperature capability of titanium alloys has evolved from about 300°C to 550-600°C today. Concordantly, the temperature capability of the turbine section has increased from about 700°C in the 1950's to about 1100-1200 °C at
present. The enhancement of temperature capability has been brought about by the adoption of new classes of materials [1], and this increase in temperature capability of the different stages of the gas turbine engine has resulted in increased thermal efficiency and better performance. Figure 1.1 shows the evolution of materials use in gas turbine engines since about 1960 and the predicted trend for the introduction of new materials [2]. To start out with, a large amount of steel and aluminium was used, but these materials have now been supplanted by nickel and titanium. Aluminium, used in the front part of the engine, has been largely replaced by high-strength low density titanium-base alloys; whereas in the rear of the engine, in the turbine section, nickel-base materials have replaced steel [3] (see Figure 1.2.) Over half a century of research and development in turbine section alloys has culminated in highly versatile alloys such as CMSX-4 and PWA 1484 and the gas turbine engine relying upon such materials has become the workhorse of 20th century aviation.

The development of Ni-base superalloys has proceeded along two major paths, one for very strong, fatigue and fracture-resistant materials for turbine discs with a relatively lower temperature capability (700–750°C) and the other directed toward high-temperature capability (1100°C or more) through cast alloys for turbine blades. The industry norm for the former was set by the emergence of alloy Inconel718 in the late 1950s. More recently evolved versions obtain higher strengths through increased alloying. The development of the cast superalloys presents a metallurgical story that contains all of the elements of classical physical metallurgy, starting with the discovery of precipitation-hardening, the use of solid-solution strengthening with refractory elements, the strengthening of grain boundaries with strengtheners, the elimination of unfavourably oriented grain boundaries by directional solidification during the investment casting process and finally the elimination of grain boundaries themselves through single-crystal
growth processes. Each phase represents a milestone in superalloy technology and the benefits have been manifold. The development of technology has proceeded with such a rapid pace that within a span of 50 years or so, we are nearing the upper limit of the capability of these materials, namely, the melting point. Any further advances in this current class of materials would therefore depend upon a sound understanding of the physical processes that govern the performance of these alloys and our ability to alter the characteristics based upon this knowledge. This has become the theme for much of the current work on nickel–base superalloys. The work presented in this thesis is aimed at gaining a better understanding of solidification during the casting process with the goal of developing a model for predicting microsegregation behaviour of nickel–base single crystal superalloys. The work looks at an experimental alloy, RR-2100 designed by Rolls-Royce plc, to be used as a possible turbine blade material. The location of the turbine blades in a modern aircraft gas turbine engine [3] can be seen in Figure 1.3.

1.2 Thesis Outline

The present chapter introduces the reader to the class of materials referred to as Ni–base superalloys giving a general introduction to the topic and describes their application in modern areoengines. Further chapters deal with the various individual aspects of the study. Chapter 2 presents a literature review of the current understanding of the metallurgy of nickel–base superalloys. Therein is described superalloy chemistry, the physical metallurgy of this class of materials, common processing techniques by which components such as blades are made and a review of the problem of microsegregation associated with the casting technique and the available mathematical models that describe this phenomenon. Examples of typical
Superalloys are also given with particular reference to their microsegregation behaviour. Conclusions are drawn based upon the review at the end of Chapter 2 that emphasize the need for the work detailed in this thesis. Chapter 3 details the experimental procedures employed in order to achieve the goal of this work and Chapter 4 presents the results from the experiments carried out. A description of the mathematical model employed in this study to characterize microsegregation in Ni-base single crystal superalloys can be found in the latter. Chapter 4 also presents a detailed discussion of the results and their interpretation presents an explanation for the findings. Finally Chapter 5 draws conclusions from this work and recommendations are made for further investigation.

1.3 Justification and scope

Superalloys have developed rapidly over the past few decades and their capabilities have exceeded those of other classes of materials. The drawback however, is that our understanding of the physics of this class of materials has not kept pace with the developments. Current alloys have the capability to function at temperatures close to their melting point and with constant changes in alloy chemistry, the design, production and subsequent performance of these alloys has been qualified by our incomplete understanding thereof. With the availability of powerful computers, it is now possible to carry out calculations both with efficiency and economy that simulate different aspects such as alloy design, processing, casting, heat treatment and subsequent performance in service of various components made of superalloys, and since detailed experiments are both expensive and involved, much of the current focus has been directed towards gaining an understanding of each of the aspects listed above from a physical standpoint. With the help of detailed and accurate mathematical models resulting from
this understanding it is expected that future alloys would exceed the capabilities of the ones currently in use. The work carried out in this thesis forms a part of this larger aim.

The aim of this thesis is to understand the phenomenon of microsegregation in castings during solidification. The scope of the thesis therefore consists of carrying out experiments with a suitable Ni–base single crystal superalloy, characterizing the solidification conditions and obtaining meaningful data of composition which could be understood with a reliable mathematical model. It is expected that such a study should not only further our understanding but also impact alloy design and manufacturing.
Figure 1.1 Evolution of materials use in aeroengine turbines (after [2]).

Figure 1.2 The location of materials within the gas turbine engine (After [3]).
Figure 1.3 Artist's impression of a gas turbine engine, the turbine blades are indicated (after [3]).
Chapter 2

Literature Review
2.1 The Metallurgy of the Ni-base Superalloys

Nickel–base superalloys contain many alloying elements to make them suitable as high temperature materials. Superalloy components can perform well at temperatures close to the melting temperature of the alloy. Ni–base superalloys account for about 50% of the weight of the modern aircraft engine. Present day alloys may contain 10 or more elements added for various reasons to Ni which forms the matrix phase called gamma (\(\gamma\)). The classification of these alloying elements and their alloying amount depends upon the phases present in the alloy system. The important phases that are required to be present for high-temperature applications are as follows [1]:

a) **Alloy Matrix** (\(\gamma\)): The Gamma phase forms the matrix. It is a Face Centred Cubic (FCC) austenitic phase. It usually contains several elements like Co, Cr, Mo, W etc in solid solution. Even though nickel by itself does not possess good resistance to rupture and/or creep, the austenitic matrix is favoured by alloy designers because of the following reasons:
   - High tolerance of nickel for alloying without phase instability because of electron vacancies in the d-shell.
   - Tendency to form protective oxide scales in particular with chromium addition.
   - The tendency to form alumina rich oxide scale at high temperatures which imparts good resistance to oxidation.

b) **Gamma Prime** (\(\gamma'\)): This is a FCC precipitate phase falling under the category of A_3B compounds. It acts as the primary hardening agent in nickel–base superalloys and is of great engineering significance. A high-nickel matrix favours the precipitation of \(\gamma'\), which has a high
degree of coherency with the matrix. In the \( \gamma' \)-type \( A_3B \) compound relatively electronegative elements, such as Ni, Co, or Fe, compose the “A”, while more electropositive elements like Al, Ti, or Ta compose the “B”. Thus, typically in a nickel-base superalloy \( \gamma' \) could have the chemical formula \( (\text{Ni, X})_3(\text{Al, Y}) \) where \( X = \text{Co, Cr, Fe etc, and Y = Ti, Ta, Fe, Cr, Mo etc} \) [4].

The \( \gamma' \) phase imparts strength by acting as a hardening agent in the matrix, thus it is desirable to have significant amounts of this phase in the alloy system. Modern alloys can have as much as 70% by volume of \( \gamma' \) [5,6]. It has a primitive cubic \( \text{L1}_2 \) crystal structure as shown in Figure 2.1, with the Al atoms forming the cubic crystal and the Ni atoms located at the face centers. The ordering temperature of \( \gamma' \) is close to its melting temperature, making it suitable for high temperature applications. The \( \gamma' \) phase contributes to strengthening of the \( \gamma - \gamma' \) alloy by interacting with dislocations and forming anti-phase boundaries (APB's) [7-9] which are the faulted regions between two partial dislocations traveling in the \( \gamma' \) phase. The dislocations enter the \( \gamma' \) phase by shearing through [8,11] and the Orowan process [10] does not operate when this happens.

c) **Carbides**: Carbon is added with the objective of forming grain-boundary carbides which improve the strength of the grain boundaries at high temperatures by pinning dislocations and inhibiting grain boundary sliding [12]. Examples of carbide forming elements are Cr, Mo, Nb, Ti, Ta, and W [13].

d) **Grain Boundary \( \gamma' \)**: Commonly found in modern disc alloys, this phase is formed during heat treatment which generates a film of \( \gamma' \) along the grain boundaries serving to enhance the rupture properties. This
treatment results in a complex distribution of precipitate particles; for a schematic illustration refer to Figure 2.2. Research has shown that yield stress in disc alloys is controlled by particle shearing, and an optimum distribution of the precipitates yields best properties [14].

Based upon the phases present in an alloy, the alloying elements can be classified into three main categories with two sub-categories. The first category of elements are called $\gamma$-formers, which reside in the austenitic matrix phase and serve to stabilize and strengthen its disordered FCC structure. Examples of such elements are Co, Fe, Mo and W. The second category of elements are the so called $\gamma'$-formers. These elements have a tendency to form ordered precipitates having the L1$_2$ structure. Al, Ti, Nb and Ta are examples of $\gamma'$-formers. The third group of elements that are used in superalloys are the grain boundary stabilizers and strengtheners. Commonly used elements of this type are B, Hf, Zr etc. The two sub-categories of elements are first, those that form oxide scales imparting corrosion and/or oxidation resistance such as Al and Cr [15] and second, those that form carbides. The carbide forming elements have been discussed earlier in the text. Table 2.1 gives a brief summary of the reasons for the addition of different elements to a nickel-base superalloy, their primary effects as well as any secondary and undesirable effects.

Modern nickel-base single crystal superalloys additionally contain large amounts of refractory elements such as Re, Ta, Ru and W [16,17]. In alloys that contain such large fractions of refractory elements (7 wt % or more [1]) there is a tendency for the precipitation of undesirable Topologically Close-Packed (TCP) phases. These phases have complex structures and are rich in Ni, Cr, Mo, Co, W and Re which are elements that impart solid solution strengthening and good creep resistance [18]; thus precipitation depletes the matrix of these elements resulting in deteriorated alloy properties. TCP's
phases can precipitate in a variety of shapes and have weak and incoherent interfaces with the γ/γ' matrix which is deleterious as it can result in easy fracture [19]. Moreover, the precipitation of TCP's at elevated temperatures is frequently accompanied by the formation of voids in the matrix which may potentially act as fracture initiation sites [20]. It has also been shown that Ru–containing alloys are also prone to TCP formation [21-23].

<table>
<thead>
<tr>
<th>Element</th>
<th>Matrix Strengthening</th>
<th>Effect on % precipitates</th>
<th>Carbides</th>
<th>Other effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>Moderate</td>
<td>Moderate</td>
<td>M23C6 &amp; M7C3</td>
<td>Improved corrosion resistance, promotes TCP formation</td>
</tr>
<tr>
<td>Mo</td>
<td>High</td>
<td>Moderate</td>
<td>M6C &amp; MC</td>
<td>Increased density</td>
</tr>
<tr>
<td>W</td>
<td>High</td>
<td>Moderate</td>
<td></td>
<td>Promotes TCP's</td>
</tr>
<tr>
<td>Ta</td>
<td>High</td>
<td>High</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>High</td>
<td>High</td>
<td>NbC</td>
<td>Promotes γ''† and δ phases</td>
</tr>
<tr>
<td>Ti</td>
<td>Moderate</td>
<td>Very High</td>
<td>TiC</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Moderate</td>
<td>Very High</td>
<td></td>
<td>Improved oxidation resistance</td>
</tr>
<tr>
<td>Fe</td>
<td>Moderate</td>
<td>γ'→β,η</td>
<td></td>
<td>Decreases oxidation resistance, promotes TCP's</td>
</tr>
<tr>
<td>Co</td>
<td>Moderate</td>
<td>Moderate</td>
<td></td>
<td>Raises Solidus</td>
</tr>
<tr>
<td>Re</td>
<td>Moderate</td>
<td></td>
<td></td>
<td>Improves creep by retarding coarsening but increases lattice misfit</td>
</tr>
<tr>
<td>Ru</td>
<td></td>
<td></td>
<td></td>
<td>Increases liquidus, promotes TCP's</td>
</tr>
<tr>
<td>B, Zr</td>
<td>Moderate</td>
<td></td>
<td></td>
<td>Grain boundary strengthening, inhibit carbide coarsening, and improve creep strength and ductility</td>
</tr>
</tbody>
</table>

Table 2.1 Effects of alloy additions to nickel-base superalloys

† The γ'' phase is an undesirable tetragonal phase e.g. Ni₃Nb
Apart from TCP formation the other problem associated with the addition of refractory elements is that thermo-solutal convective instabilities may set in during solidification and result in defects such as freckles [24,25]. Since the compositions of modern single-crystal superalloys are characterized by significant additions of refractory elements for improved creep resistance, it thus becomes necessary to understand and to reliably predict the solidification characteristics of different alloy compositions and much of the current work in superalloys is directed towards this goal.

Over circa 50 years, there has been considerable development of alloys and a vast number of them have been developed for specific applications. Broadly speaking, nickel-base superalloys can be classified into two classes, namely, wrought and cast alloys. The wrought products are used in turbine discs and combustor cans, while products having intricate geometrical shapes such as blades of the turbine and compressor sections and nozzle guide vanes are made via the casting route. Cast alloys can be further classified as equiaxed, directionally solidified (DS) and single crystal (SC or SX). Table 2.2a shows the composition of different wrought alloys while Table 2.2b shows several cast single crystal alloys and their compositions.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Mn</th>
<th>Fe</th>
<th>Al</th>
<th>Ti</th>
<th>Ta</th>
<th>Cb</th>
<th>B</th>
<th>W</th>
<th>Zr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hastalloy C276</td>
<td>0.02</td>
<td>2.5</td>
<td>14.5-15.5</td>
<td>15.5</td>
<td>1</td>
<td>4-</td>
<td>7</td>
<td>1</td>
<td>4-</td>
<td>7</td>
<td>3-</td>
<td>4.5</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>Waspaloy</td>
<td>0.05</td>
<td>13</td>
<td>19.5</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>1.4</td>
<td>3</td>
<td>0.01</td>
<td>0.07</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Astroloy</td>
<td>0.04</td>
<td>17</td>
<td>15</td>
<td>5</td>
<td>4</td>
<td>3.5</td>
<td>0.025</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inconel X - 750</td>
<td>0.08</td>
<td>13</td>
<td>14-15</td>
<td>0.3</td>
<td>5-</td>
<td>0.4-</td>
<td>2.25-2.7</td>
<td>0.8</td>
<td>0.3</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2a Composition of various wrought Ni-base superalloys, in wt. pct.
As can be seen the compositions vary considerably depending upon the particular alloy. For example Waspaloy and Hastalloy C-276 are wrought nickel-base alloys and both contain grain boundary strengthening elements such as C, B, or Zr. Whereas in single crystal alloys such as CMSX-4 or RR-3000 there is no need for grain boundary strengtheners, as grain boundaries are absent in components made of these alloys. Since DS and SX alloys are used for making turbine blades where the prime requirement is creep resistance and strength, they naturally have more γ' present in them. As a result cast alloys have a greater fraction of γ'-forming elements as compared to wrought alloys which typically have greater amounts of solid solution strengtheners such as Mo; Hastalloy C-276 has as much as 15-17 wt. percent Mo added to it for the purpose of strengthening the γ matrix, however it cannot be added in any significant quantities to cast alloys as it has been observed to be a promoter of TCP’s [18,26]. It can also be seen that refractory elements such as Re, W, Ru, Ta etc. are absent from wrought alloys. Such elements provide considerable creep resistance and strength and are required only in turbine blade alloys which operate at temperatures in the vicinity of 1100°C-1200°C. Although significant amounts of these refractory elements are present in cast alloys there remains a danger of TCP formation at higher temperatures. It has however been observed that by increasing the amount of cobalt there is a decrease in the rate of the TCP σ-phase nucleation [18]. Re

Table 2.2b Composition of various single crystal Ni-base superalloys, in wt. pct.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Ru</th>
<th>Fe</th>
<th>Al</th>
<th>Ti</th>
<th>Ta</th>
<th>Re</th>
<th>B</th>
<th>W</th>
<th>Zr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMSX-4</td>
<td>9–6.5</td>
<td>6.5–6.7</td>
<td>0.5–0.6</td>
<td>5.6–5.7</td>
<td>1</td>
<td>6.4–6.5</td>
<td>3</td>
<td>6–6.4</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PWA-1484</td>
<td>10</td>
<td>5</td>
<td>1.9–2</td>
<td>5.6–5.65</td>
<td>8.7–9</td>
<td>3</td>
<td>5.9–6</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RR-3000</td>
<td>3</td>
<td>2</td>
<td>0.03</td>
<td>5.7</td>
<td>0.2</td>
<td>8</td>
<td>6</td>
<td>5</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RR-2101</td>
<td>12</td>
<td>2.5</td>
<td>2</td>
<td>6</td>
<td>5.5</td>
<td>6.4</td>
<td>9</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As can be seen the compositions vary considerably depending upon the particular alloy. For example Waspaloy and Hastalloy C-276 are wrought nickel-base alloys and both contain grain boundary strengthening elements such as C, B, or Zr. Whereas in single crystal alloys such as CMSX-4 or RR-3000 there is no need for grain boundary strengtheners, as grain boundaries are absent in components made of these alloys. Since DS and SX alloys are used for making turbine blades where the prime requirement is creep resistance and strength, they naturally have more γ' present in them. As a result cast alloys have a greater fraction of γ'-forming elements as compared to wrought alloys which typically have greater amounts of solid solution strengtheners such as Mo; Hastalloy C-276 has as much as 15-17 wt. percent Mo added to it for the purpose of strengthening the γ matrix, however it cannot be added in any significant quantities to cast alloys as it has been observed to be a promoter of TCP’s [18,26]. It can also be seen that refractory elements such as Re, W, Ru, Ta etc. are absent from wrought alloys. Such elements provide considerable creep resistance and strength and are required only in turbine blade alloys which operate at temperatures in the vicinity of 1100°C-1200°C. Although significant amounts of these refractory elements are present in cast alloys there remains a danger of TCP formation at higher temperatures. It has however been observed that by increasing the amount of cobalt there is a decrease in the rate of the TCP σ-phase nucleation [18]. Re

15
has proven to be valuable for imparting enhanced creep resistance [27-29], thus over the years three generations of cast superalloys have emerged characterized by progressively increasing rhenium content. The improvement in creep resistance stems from the retardation of diffusional $\gamma'$ coarsening at high temperatures due to rhenium, this promotes a faster transition to the strain dependent directionally coarsened rafted structure [30]. This has been demonstrated by investigators in Ref. [31]. Correspondingly, the amount of chromium has decreased with increase in rhenium, as the latter has a higher tendency to form TCP precipitates in the presence of chromium [28,32]. Chromium is beneficial as it forms a protective oxide scale imparting corrosion resistance [33,34], but manufacturers prefer to make modern blade alloys more resistant to oxidation than corrosion by increasing the aluminium content. In addition to increasing the aluminium content manufacturers have also increased the amount of tantalum as it has been observed to not only strengthen the $\gamma$ and $\gamma'$ phases but also improves ductility [35]. Since the amounts of rhenium and tungsten have increased in modern cast SX alloys the amount of tantalum has also been correspondingly increased as it is observed that by lowering the ratio of the amount of rhenium and tungsten combined to tantalum, below a critical value of 1.25, the resistance to freckling increases [36], as tantalum serves to restrict the density inversion resulting in freckling by segregating strongly to the liquid phase [37]. With the need to enhance high temperature performance the amount of cobalt has also undergone an increase as it raises solidus and provides solid-solution strengthening [38], it is due to this reason that alloys such as Waspaloy have as much as 20 wt. percent cobalt. To summarize, modern superalloys contain several different alloying elements and their relative amounts are dictated by the specific application for which the alloy is to be designed. Superalloys have complex chemistry and the effects of these alloying elements on the properties of the alloys are not yet completely understood.
As the work contained in this thesis deals with cast single crystal alloys, ergo, discussion of alloy production will be limited to cast alloys. A discussion on the problems associated with casting methods can be found in § 2.3 and the phenomenon of microsegregation is addressed in § 2.4. Finally, the chapter is concluded with a brief overview of the discussion.

2.2 Process Metallurgy – Alloy Production

Today’s engine material requirements are so stringent that in order to produce alloys for aircraft engines and land–based gas turbines a number of different melting procedures are combined with precise and state of the art forming techniques. The physical metallurgy of superalloys demands the highest degree of process consistency; thus alloy manufacturers have to exercise every method of control at their command. The first step in the processing route is the manufacturing of ingots for subsequent re–melting. These ingots are usually produced by melting together pure metals and refined and unrefined scrap using vacuum induction melting (VIM), making cylindrical rods. The use of vacuum inhibits the formation of oxide and nitride inclusions, at the same time impurities such as Pb and Bi are volatilized and driven out of the system [39]. Following VIM, the ingots still have gross segregation and though quite clean, still have refractory impurities i.e., non-metallic inclusions. These ingots are then subjected to secondary melting processes, viz., vacuum arc re–melting (VAR) or electro–slag re–melting (ESR). These operations reduce the number of inclusions and lead to the production of very clean ingots and billets for either subsequent forming operations to make completed end products such as turbine discs or for subsequent re–melting into cast components such as turbine blades.
The investment casting technique employed for making turbine blades of complex geometries is outlined below.

2.3 Investment Casting

The basic investment casting process (also known as the lost wax process) has remained unchanged for centuries, but major refinements have taken place since the late 1920’s when production of dental components sparked off innovations that ultimately led to the first superalloy applications [40]. Gas turbine airfoils have since then become the single most important application of this technology. First, an exact pattern of the part to be produced is made of ceramic. The pattern material (wax or plastic) is then injected around a preformed ceramic core inserted in the die cavity. The ceramic core mimics the internal passages (for air flow) in a turbine blade. The moulds are produced by immersing the pattern assembly in aqueous ceramic slurry. Following this, the shell is coated with a layer of granular ceramic stucco which serves to strengthen the shell. More layers of the coating are added until the required strength is obtained. Thence, the wax is melted out of the shell and the mould is fired to make it strong enough for handling and storage. Single crystal castings are produced using vacuum casting equipment. After the metal is poured, the mould is withdrawn from the hot zone of the furnace at a predetermined rate which determines the microstructure of the component [41-43]. The primary dendrite growth direction is confined to the $<001>$ direction by a geometrical constriction to the advancing grain growth in the form of a chicane – a narrow necked diaphragm or a helix [5], see Figure 2.3. When the growth front reaches the constriction the number of grains is reduced to a single one growing close to the $<001>$ direction, refer to Figure 2.4. During growth in the grain selector several grains oriented in different directions compete with each other; the
survival of a single grain close to the <001> stems from the fact that this
crystal direction has the highest growth rate parallel to the withdrawal
direction and thermal gradient [44-46]. It is fortuitous that the preferred
growth direction is <001> for it is also the direction having the minimum
value of Young's Modulus and thus has shown to offer the highest creep and
fatigue resistance [47,48]. Deviations from the <001> direction are common
and in practice a maximum of 10° away from the <001> direction is deemed
tolerable in final blades depending upon the exact specifications of the blade.

An unavoidable consequence of the investment casting process however, is
the presence of microsegregation. This is an effect of the dendritic growth of
the advancing solidification front, as the mould/component is withdrawn from
the furnace [49]. Microsegregation results in an uneven distribution of solute
elements in the casting and as a result the thermal and mechanical
properties of the component are not homogeneous. This phenomenon and its
consequences are discussed in the following section.

2.4 Microsegregation

Development of directional solidification was motivated by an effort to control
the morphology of grain boundaries so that fracture resistance may be
improved. Subsequently, this technology was applied successfully to produce
single crystal gas turbine blades. Such a morphology in castings has
significantly improved the high temperature mechanical properties of
superalloys [1]. The strength of superalloys is contingent upon several factors
working together, such as solid-solution strengthening, volume fraction of
gamma prime, morphology and size of precipitates etc., and these factors all
are ultimately controlled by the chemical composition of each phase. Thus, in
order to obtain optimum mechanical and thermal properties, knowledge of
microsegregation processes resulting in uneven distribution of solute becomes necessary.

Microsegregation is a phenomenon attendant with directionally solidified dendritic structures [50]. It results from solute redistribution during dendritic solidification and leads to a continuous variation in the solute concentration between the center and the outside of a dendrite arm, this is called coring. This variation in solute concentration is found to have a periodicity dependent on the scale of the dendritic structure [51-53]. Thus, the scale of the dendrites and the degree of solute heterogeneity are significant for optimizing properties of the component. Figure 2.5a shows the typical morphology of dendritic growth in a superalloy and Figure 2.5b shows the complex nature of the concentration profiles as determined by electron probe microanalysis in a different study by the authors in Ref. [54]. These clearly reflect the anisotropic morphology of dendritic growth and evidence of coring is visible in the EPMA map of a strongly segregating element such as rhenium. It can also be seen that microsegregation is quite severe in this alloy. A component with such a great degree of microsegregation cannot be used in service without proper heat treatment to homogenize the composition.

Since dendrite arm spacing defines the range of microsegregation, measurements of the arm spacing have been related to solidification conditions [55,56] and were linked with the local solidification time [57] (defined as the time at a given location in the casting or ingot that is allowed for the solidification process from initiation to completion or near completion). The local solidification time is inversely proportional to the average cooling rate at the particular location. The primary dendrite arm spacing ($\lambda$) has been found to depend upon the temperature gradient and the withdrawal rate, in general the following relationship is found to exist [42,58-60]:
\[ \lambda_1 = C \cdot G^{-m} \cdot R^{-n} \]  

where \( G \) is the temperature gradient and \( R \) is the withdrawal speed and \( C \) is a constant which was found to depend upon the solidification characteristics resulting in secondary dendrite arms; if the secondary arms coarsened more then the proportionality constant increased [61]. The investigators in Ref [61] found that the superalloy PWA 1484, which is a multi–component alloy, could be modeled as a pseudo–binary alloy, and observed that the measured primary dendrite arm spacings agreed well with Eq. 1, the values of exponents being \( m = 0.5 \) and \( n = 0.25 \). Typical primary dendrite arm spacings observed in directionally solidified single crystal superalloys are on the order of 100–350 \( \mu \)m [62].

The first work to characterize the distribution of solute elements during directional dendritic solidification was carried out by Gulliver [63] in 1913 and later derived by Scheil [64] in 1942 and by Pfann [65] in 1952. The equation thus derived is now known as the “classical non–equilibrium solidification equation”. On the other hand, equilibrium solidification occurs under conditions of thermodynamic equilibrium at all times, thus any thermal or compositional gradients are eliminated. If such conditions prevail, the composition of each phase is uniform and remains unchanged during the entire solidification process from start to finish. This behaviour can then be described by the classical lever rule which applies for linear liquidus and solidus lines:

\[ C_s = C_s^i = \frac{kC_0}{f_s(k-1)+1} \]  

Eq. 2
where \( C_s \) is the solid composition, and the superscript \( i \) refers to the composition at the solid–liquid interface, \( C_0 \) is the composition of the bulk, \( f_s \) is the fraction solidified and \( k \) is the partition coefficient. The value of the partition coefficient determines to which phase the solute segregates. If \( k < 1 \), then the solute partitions towards the liquid phase, if \( k > 1 \), then the solid gets enriched in solute [66]. Nickel–base superalloys contain many alloying additions and the partitioning coefficients of common turbine blade alloying elements are listed in Table 2.3 [67].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Al</th>
<th>Ti</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>Co</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMSX-4</td>
<td>0.9</td>
<td>1.05</td>
<td>0.86</td>
<td>0.67</td>
<td>0.86</td>
<td>1.31</td>
<td>0.67</td>
<td>1.05</td>
<td>1.66</td>
</tr>
<tr>
<td>RR3000</td>
<td>0.9</td>
<td>1.04</td>
<td>0.69</td>
<td>0.51</td>
<td>1.08</td>
<td>1.73</td>
<td>0.85</td>
<td>1.13</td>
<td>1.97</td>
</tr>
<tr>
<td>SRR99</td>
<td>0.9</td>
<td>1.33</td>
<td>0.61</td>
<td>0.71</td>
<td>-</td>
<td>1.38</td>
<td>0.9</td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3. Experimentally determined partition ratios for three turbine blade alloys (after [67]).

Often in practice, however, it is not possible to have the entire solidifying system under thermodynamic equilibrium, although it may be reasonably assumed that equilibrium holds at the solid–liquid interface [66]. Unlike equilibrium solidification, where diffusion is complete both in the solid and liquid phases whereby eliminating composition gradients, a complementary limiting case is where diffusion is complete only in the liquid phase with no diffusion in the solid phase. This is described by the classical non-equilibrium solidification equation and can be written as:

\[
C_s' = C_0 k (1 - f_s)^{k-1} = k C_i
\]

Eq. 3

which is also known as the Gulliver–Scheil equation derived originally under the assumptions [63–65] that:
1) There is complete mixing in the liquid phase and no mixing in the solid.

2) Equilibrium holds at the solid–liquid interface, and the partitioning coefficient applies at the interface and remains constant throughout solidification.

Although the above equation was originally derived for a solidifying bar, the derivation is readily applicable to the solidification process in a directionally solidified casting or ingot modeling the space between two adjacent dendrites arms as a bar, shown schematically in Figure 2.6.

The Gulliver—Scheil equation is applicable to a volume element provided the following assumptions in addition to the ones given above hold [68]:

1) There is no mass flow in or out of the volume element.

2) There is negligible undercooling before nucleation or from curvature or kinetic effects.

In practice however, neither of the two limiting cases described by the lever rule or Scheil equation are prevalent in solidifying systems. Thus, the theoretical predictions do not agree with the final distribution of solute elements in castings and ingots. Brody & Flemings [68] pointed out in 1966 that this disagreement between the observed and the predicted values of microsegregation was due to the invalid assumption of zero diffusion in the solid. Additionally, the assumption of a constant partitioning ratio \( k \) throughout the solidification is not valid in alloy systems where the liquidus and solidus lines are not straight lines, which is the case in most multi-component alloy systems. Solute transport by diffusion in any system serves to iron out the concentration gradient. Solute is transported from regions of higher concentration to those of lower concentration. Thus, in a directionally
solidified bar as described above, there should be mass transport not only in the liquid phase but also in the solid phase, which would serve to reduce the degree of microsegregation set up during solidification. Diffusion processes are assumed to be complete in the liquid phase, which is a reasonable assumption given the greater diffusivity of solute atoms in the liquid. In the solid phase, however, given the local solidification time at a particular location in the arm space, diffusion processes may or may not be complete depending upon the diffusivity of a particular solute atom in the solvent and on the concentration gradient set up in the solid due to the magnitude of the partitioning coefficient. Redistribution of solute elements in the solid phase by diffusion is referred to as back-diffusion [68]. A brief synopsis of the model describing this phenomenon, developed by the authors in Refs. [68,69] is given below.

*The Brody - Flemings Model and its modification by Clyne & Kurz.*

The alloy system considered by Brody & Flemings was Al·4.5 pct Cu alloy [68]. The appropriate portion of the Al-Cu phase diagram is shown in Figure 2.7 drawn using Thermocalc [70]. They modeled the dendritic growth to be unidirectional having planar isotherms perpendicular to the growth direction. The dendrites were assumed to be plate like in morphology, thus the volume element had simple planar geometry. In addition to the previously noted four assumptions they assumed that:

1) Solute transport within the solid phase occurs by volume diffusion and the diffusion coefficient, \(D_s\), may be a function of temperature and/or composition, i.e., \(D_s = f(T,C_s)\)

2) The rate of thickening of the dendrite plates is a continuous function:
   constant growth rate: \(\frac{d\lambda_i}{d\theta} = u\)
parabolic growth rate: \[ \frac{d\lambda_i}{d\theta} = \frac{w}{2\sqrt{\theta}} \]

where \( u \) and \( w \) are constants, \( \theta \) is the time variable and \( \lambda_i \) is the position of the moving solid–liquid interface within the volume element (see Figure 2.8).

3) Liquid and solid densities are equal and are constant throughout solidification, hence volume changes on the diffusion path length in the solid are neglected.

By conserving solute within the volume element Brody & Flemings were able to derive expressions for the interface solid composition as a function of the fraction solidified. Their analysis yielded:

\[ C_s = kC_0 \left[ 1 - \frac{f_s}{1 + \alpha k} \right]^{k-1} \text{; for } \frac{d\lambda_i}{d\theta} = \text{const.} \]

\[ C_s = kC_0 \left[ 1 - (1 - 2\alpha k)f_s \right]^{k-1} \text{; for } \frac{d\lambda_i}{d\theta} \propto \frac{1}{\sqrt{\theta}} \]

where \( \alpha \) is the Fourier Number defined as:

\[ \alpha = \frac{D_s \theta_f}{L^2} \]

\( \theta_f \) is the local solidification time and \( L \) is the half arm spacing.

The solution of the mass balance equation (Eq. 4) however, overestimates the amount of back–diffusion, a more realistic description of the solute profile is obtained through a solution of Fick's second law for diffusion which states that the rate of change of concentration in a volume element within the diffusional field, is proportional to the rate of change of concentration gradient at that point in the field. Brody & Flemings describe a time–explicit finite difference scheme for this solution. A plot of fraction solid vs.
temperature obtained by Brody & Flemings from such a scheme is shown in Figure 2.9. It can be seen that the finite difference prediction lies between the two extremes of the lever rule and the Scheil equation indicating the effect of back-diffusion. Although the model developed by Brody & Flemings predicts the changing solid composition during solidification a number of critical observations qualified the model's application. Flemings et al. [71] and Clyne & Kurz [72] observed that the model did not conserve solute. At large values of the diffusion parameter $\alpha$, the model predicts that the temperature at which the final solid fraction freezes lies above the equilibrium solidus, or in other words the final solid to form has a solute concentration lower than the bulk composition $C_0$. Although it was observed by Brody & Flemings that the overestimate in back diffusion resulted from an approximation for the concentration gradient in the solid at the interface [69,71], the authors in Ref. [72] concluded by deriving the model differently (see Figure 2.10) that this approximation was not the source of error in the model.

Clyne & Kurz showed that the model became invalid because the condition that the diffusion boundary layer should be much lesser than the half-arm spacing ($\delta_s << L$) which is one of the precepts of the model, did not hold at large values of $\alpha$. At large values of $\alpha$, the area designated $A_3$ in Figure 2.10 would be quite large and consequently the diffusion boundary layer, $\delta_s$ would be a significant fraction of the half arm spacing, $L$. As a result, a part of this area will lie outside the physical limits of the system. In such a situation an area representing a part of the back diffusion solute will be cut off by the system limits. By considering the change in composition difference (between the pre-existing profile and that after the incremental interface advance) with distance behind the interface, Clyne & Kurz modified the diffusion parameter. Upon replacing $\alpha$ in Eq. (4) by a parameter $\beta$ defined as:
\[ \beta = \alpha \left(1 - \exp\left(-\frac{1}{\alpha}\right)\right) - \frac{1}{2} \exp\left(-\frac{1}{2\alpha}\right) \]  

Eq. 6

the Brody–Flemings model predictions are found to lie between the equilibrium and Scheil limits over a wide range of values of \( \alpha \) ranging from very small (~0.01 or less) to very large (~100 or more). The solid solute profile is approximated in this case using an exponential decay curve. Ohnaka [73] proposed a model based upon a similar modification to the solid solute profile in 1986, in this case the solid solute profile was assumed to be quadratic instead of exponential and the corresponding modified diffusion parameter \( \beta \) is given by:

\[ \beta = \frac{2\alpha}{1 + 2\alpha} \]  

Eq. 7

Kobayashi [74] developed an analytical solution for microsegregation in the case of parabolic solid growth for dendritic structures. All of the above models [68–74], assume that the liquid is well mixed and model the solute redistribution based upon diffusion in the solid phase; in systems where the solidification time is sufficiently long. However, in systems in which the solidification time is rather small, on the order of a few seconds at most, as in rapidly solidified metals [75–78] diffusion in the liquid phase may be incomplete as well. In such systems it becomes important to acknowledge the rate of diffusion in the liquid [68] wherein the diffusion of solute in a direction parallel to the growth direction can be considered to occur at a finite rate. Later models described the effect of dendrite tip undercooling on the solute concentration gradients ahead of the tips [79–82], using it to account for microsegregation. Flood & Hunt [83] proposed a “truncated Scheil” method accounting for dendrite tip undercooling resulting from a finite rate of solute diffusion in the liquid phase, they calculate a tip temperature which
is then used in a standard Scheil model giving the solute concentration at the tip corresponding to a particular solid fraction at that temperature, behind the tip, the solid fraction in the dendrite follows the Scheil prediction. This method was later modified to conserve solute in a volume element [84]. Other numerically more rigorous models [85,86] are available but the computational procedures were observed to be cumbersome for use in microsegregation prediction in a combined heat and mass transfer analysis of a casting. Tong and Beckermann [87] presented an analytical model based on the diffusion taking place in the boundary layer both in the liquid and in the solid phase. They proposed a solutal Fourier number $\beta$ for the liquid defined identically to $\alpha$, the solutal Fourier number for the solid phase. The derivation is based upon solute conservation within a volume element in the half-arm spacing. The results of their model were in better agreement with experimental data obtained by the authors in Ref [88] on an Ag-Cu alloy in comparison to other models. However, the model does not agree perfectly with the experimental data for solid fractions greater than about 0.75. Nevertheless, the model reduces to the Scheil and Lever rules respectively under limiting conditions and addresses solute diffusion in the liquid phase quite effectively.

Most of the models outlined above pertain to binary systems, the first analytical approach to describe a ternary system was carried out by Mehrabian & Flemings [89], later, a numerical model based on microsegregation coupled with phase diagram calculations for multi-component alloy systems was developed [90]. Models of microsegregation for binary alloys are somewhat simpler; they do not involve complications arising from the influence of other alloying elements that can result in changes in partitioning coefficient with temperature, with appreciable effects on the solidification path [91]. Thus, several researchers have combined phase diagram and microsegregation calculations for Al-Mg alloys [91-94] and also
for multi-component superalloys [95,96]. Although the results give predictions of solute redistribution and the advent of defects such as freckling, there is not enough experimental data for proper validation of these models.

Thus, several mathematical models are available, both analytical and numerical, that address the phenomenon of microsegregation. The predictions of these models have been found to be reasonably accurate with regard to specific systems and solidification conditions. However, experimental evidence for back diffusion in modern superalloys is scarce and model predictions of microsegregation in these systems are qualified by the available thermodynamic databases that are necessarily approximate owing to the complex chemistry of these alloys. Thus there is a two-fold need for firstly obtaining experimental evidence for back diffusion so that the present models may be tested and improved, secondly there is a need for carefully targeted experiments to make available more accurate thermodynamic databases. It is to be noted however, that the latter is outside the scope of this thesis.

2.5 Summary of the Literature Survey

The literature survey presented above details the metallurgy of nickel – base superalloys in particular, single crystal superalloys. A brief description of the process metallurgy and the casting technique is also given. The phenomenon of microsegregation associated with the casting process resulting in undesirable compositional heterogeneities in the component is described with specific attention to different models for predicting this behaviour. The drawbacks of the various models were also addressed.
As an overview the following conclusions can be drawn from the preceding discussion:

The solidification process is the most important step in the processing route – presently it is the only method of producing single crystal turbine blades with economy. Thus, the problems associated with this technique ultimately determine the capability and limitations of the component. The heterogeneity in composition arising from the effects of microsegregation during solidification results in an uneven distribution of the alloying elements, which were carefully chosen in the first place to ensure optimum alloy properties, microsegregation defeats this end. However, back diffusion of solute in the solid is helpful because it serves to iron out the composition gradients and reverses the effect of partitioning. In the final component it is desirable to have a homogeneous distribution of solute elements therefore, knowledge of the degree of microsegregation becomes necessary in order to be able to subject the component to the appropriate homogenizing heat treatment procedures. Thus there is a need to have a sufficiently accurate predictive capability so that predictions of the final solute concentration profile in a casting can be obtained, given a certain set of solidification conditions and a given alloy composition. Concordantly, experimental evidence of microsegregation in different systems is also required to verify these predictions. Current research in the field of superalloys is dedicated to understanding these systems at a fundamental level, in terms of technology these alloys are state–of–the–art and consequently rather expensive to make and experiment with. Thus much of our understanding expressed in terms of models that simulate the different individual steps of the processing route – from alloy design involving choosing the appropriate alloying elements and their relative amounts to ingot production and casting to final forming of the component, will each contribute towards an integrated comprehensive model comprising of all these steps. Such an integrated model will ensure that the
production of components will be much improved and will not be subject to many of the current defects (that result in rejection of components) and yield premium performance in service. A key part of such an integrated model would be the solidification model which would be able to predict microsegregation. Microsegregation ultimately determines the occurrence of defects such as freckling, white spots etc., and determines further processing steps and therefore proper understanding of this phenomenon is critical.

Thus, the work contained in this thesis focuses on developing an understanding of the solidification process with regard to solute redistribution during solidification and obtaining experimental evidence of back diffusion in a nickel–base single crystal superalloy with the aim of arriving at a suitable model for predicting microsegregation. The following chapter delineates the experimental procedure and the methods and materials employed. The modeling is described in Chapter 4, wherein a shorter but more specific review of the literature with regard to individual aspects of the model can be found.
Figure 2.1 Crystal structures of (a) disordered $\gamma$ phase and (b) the ordered $\gamma'$ phase.

Figure 2.2 Schematic representation of different types of gamma prime precipitates.
Figure 2.3 Starter block and grain selector for casting single crystal superalloys (after [1]).

Figure 2.4 Schematic illustration of single grain selection. (After [1]).
Figure 2.5a Typical dendrite morphology in single crystal superalloys. Shown here is the dendritic structure in PWA 1484. After [61].

Figure 2.5b EPMA maps for as cast RR2071 showing microsegregation in the component. After [54].
Figure 2.6 Schematic illustration of a volume element in the dendrite arm space.

Figure 2.7 Equilibrium phase diagram of the Al-Cu binary system made using Thermocalc.
Figure 2.8 (a) Schematic diagram of mushy zone in dendritic solidification and (b) enlarged sketch of small volume element at x in the mushy zone. After [69].
Figure 2.9 Results from Ref. [69]. Plot of fraction solid versus temperature showing the effect of back diffusion.

Figure 2.10 Schematic illustration of solute redistribution during incremental freezing in a volume element of length L. After [72].
Chapter 3

Experimental Methods
3.1 Experimental Objective

The primary objective of carrying out the experiments was to test the extent to which the phenomenon of back diffusion occurs in a nickel–base single crystal superalloy.

An experimental fourth generation single crystal superalloy (RR·2100) was chosen. The alloy was supplied by Rolls-Royce plc in the as cast condition in the form of 4.5 mm diameter rods of approximate length 76.2 mm (3 in.). These had been directionally solidified according to the method described in § 2.3. Thus in each rod the dendrite growth direction was within a few degrees of the <001> crystallographic direction, which was confirmed with Laue Back Reflection [97] (see Figure 3.1). Four–fold symmetry can be seen about point O and this was confirmed to be the reflection of the {001} plane. This point is approximately 3° away from the East–West axis which is the <001> direction. Thus the dendrite growth direction was considered to be sufficiently close to the <001> direction for practical purposes.

The chemical composition of one of these rods was determined using Leco CS244 / TC436AR furnaces and inductively coupled plasma optical emission spectroscopy (ICP – OES). The results are shown in Table 3.1.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
<th>W</th>
<th>Re</th>
<th>Ta</th>
<th>Hf</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>6</td>
<td>12</td>
<td>2.5</td>
<td>9</td>
<td>6.4</td>
<td>5.5</td>
<td>0.15</td>
<td>Bal</td>
</tr>
</tbody>
</table>

Table 3.1. The chemical composition of the RR·2100 alloy used in this study.

In order to carry out directional solidification experiments for obtaining single crystal components solidified under different solidification conditions,
the solidus and liquidus temperatures as well as the solidification behaviour of the alloy were characterized using Differential Scanning Calorimetry (DSC) [98]. The following section describes the DSC experiments.

3.2 Differential Scanning Calorimetry Experiments

A small sample of the alloy was studied with DSC to determine its solidification behaviour and range. A SETARAM TGA-DTA / DSC-96 model was employed for this purpose. The crucibles used were made of $\alpha$-alumina. The sample size was kept small in order to minimize the thermal gradient within the sample [67]. Cylindrical samples of 4.5 mm diameter and 2 mm thickness were found to yield an acceptable signal-to-noise ratio. The ASTM standard test method (designation: E 1269 – 01) for determining specific heat capacity by differential scanning calorimetry was employed [99]. The test method consists of heating the test material at a controlled rate in a controlled atmosphere through a given region of interest. For the alloy RR-2100, a first approximation for the region of interest was obtained using Thermocalc [70] assuming Scheil solidification. The liquidus temperature was predicted at 1696 K or 1423 °C. Thus, the range of interest for the DSC test was taken to be 10 °C – 1500 °C. A sapphire ($\alpha$-alumina) standard of known mass and specific heat was employed as the reference material. A brief description of the test procedure is outlined below [99] (see Figure 3.2 for a schematic illustration of the test procedure):

1) The DSC apparatus was first purged with helium gas, and this was maintained throughout the experiment at a rate of 40 mL / min.
2) A clean empty sample holder (crucible of $\alpha$-alumina) was weighed to a precision of ± 0.01 mg, and the value recorded.
3) An empty specimen holder and a reference specimen holder, similarly weighed, were positioned beside one another in the DSC apparatus.

4) The DSC test chamber was cooled to the initial temperature (10 °C) for the experiment at 10 °C/min.

5) The DSC test chamber was held isothermally at the initial temperature for 4 min. to establish equilibrium. This thermal curve was recorded.

6) The test specimen was heated from the initial temperature of 10 °C to the final temperature of 1500 °C at a rate of 10 °C/min. The thermal curve was continuously recorded.

7) A steady state isothermal baseline at the peak temperature was recorded.

8) The test specimen was cooled from the peak temperature down to the initial temperature at a cooling rate of 10 °C/min and the thermal curve recorded.

9) The DSC test chamber was cooled to 10 °C.

10) The sapphire standard was placed in the reference specimen holder described in step (3) and the total weight recorded to a precision of ± 0.01 mg.

11) Steps 4 through 9 were repeated.

12) The test specimen (RR-2100 sample) was placed in the empty specimen holder described in step (2) and the total weight recorded to a precision of ± 0.01 mg.

13) Steps 4 through 9 were repeated.

The data recorded were based upon the difference in the electrical signal between the two crucibles. The amplified signal from the run with the two empty specimen holders is the baseline \((S_e)\) which represents any background signal due to the surroundings and this can be subtracted from the specimen signal. The signal \((S_c)\) obtained from the run with the empty crucible and the
sapphire standard is the calibration run; the specific heat of alumina \([100]\) is well known and by carrying out this run and comparing to the accepted values of specific heat, the instrument is calibrated to calculate the specific heat of the unknown sample. The specimen signal is obtained from the third run as \(S_s\). The specific heat of the unknown sample is then calculated using the ratio method \([67]\) as (refer to Figure 3.3):

\[
C_{ps} = \left[ \frac{(S_s - S_e)}{(S_c - S_e)} \right] \times \frac{mc}{ms} \times C_{pc}
\]

Eq. 8

where: \(C_{px}\) = specific heat, \(S_x\) = signal, \(m_x\) = mass, \(x = s\) (sample), \(c\) (calibrant) and \(e\) (empty) \([101]\).

From the determined specific heat curve (see Figure 3.4) it is possible to determine the liquidus and solidus temperatures. The width of the peak represents the freezing range of the alloy. The temperature at the onset of the peak (Point \(X\) in Figure 3.4) represents the liquidus temperature while the temperature corresponding to the stage at which the peak levels off (Point \(Y\) in Figure 3.4) represents the solidus temperature. Thus the liquidus temperature was estimated as \(1710\) K and similarly the solidus temperature was estimated as \(1633\) K, the freezing range being \(77\) K. Conversion of data from specific heat versus temperature to fraction solid versus temperature was carried out using a geometrical method \([102]\). The resulting solidification path for RR-2100 is shown in Figure 3.5. The small peak at point \(Y\) is the eutectic reaction.

It can be seen from Figure 3.5 that the solidification path as determined from the DSC experiment lies between the upper and lower limits imposed by the equilibrium and Scheil limits respectively. The equilibrium and Scheil predictions shown are calculations with Thermocalc. The DSC measurements
suggest that there is an effect of back diffusion in the solid during solidification which results in deviation of the solidification path away from the Scheil and towards the equilibrium limit [69]. Given the above observation and the determination of the freezing range of the alloy, Directional Solidification and Quench (DSQ) experiments were undertaken with the objective of observing back diffusion in the alloy during solidification. The following section describes the DSQ experiments.

3.3 Directional Solidification and Quench Experiments

The objective of these experiments was to quench the alloy after allowing it to solidify directionally so as to freeze-in the mushy zone. Examination of the quenched mushy zone would then represent a snapshot of the solidification conditions just prior to quench. Thus, any concentration gradients in the solid and the liquid would be revealed and subsequently interpreted for analyzing microsegregation at the scale of the dendrites.

A schematic illustration of the DSQ furnace, essentially a vertical configuration Bridgman furnace [103], is presented in Figure 3.6. It is an induction furnace. The water cooled copper coil is connected to a 5 kW, 450 kHz Radyne power supply. A hollow cylindrical graphite susceptor is employed for conducting heat into the specimen. The melting chamber of the furnace is first evacuated by a mechanical pump and then purged with argon gas, which is circulated through the system at a flow rate of approximately 40 mL/min throughout the course of the experiment. The cylindrical samples described in § 3.1 were lowered into the furnace at the bottom of long crucibles. These crucibles were made with a fine alumina tube (approximately 6 mm inner diameter (I.D.), 7 mm outer diameter (O.D.), and length 534 mm or 21 in.) plugged with alumina paste. The flat top plugs
(approximately 26 mm or 1 in.) were allowed to dry for over a day at 100 °C and cured at 300 °C for a day. Due to the fairly small size of the samples and complication arising from furnace design and geometry, it was not possible to monitor and collect thermal data during the runs with the actual specimens. However, temperature profiles of the furnace in the steady state were recorded with Type-D (W-3%Re/W-25%Re) thermocouples during calibration runs. The thermocouples were placed inside a tube of titanium (approximately 3.5 mm I.D., 5.5 mm O.D. and length 1500 mm or 5 ft.) which was sheathed with a plugged alumina tube described above. The titanium metal tube was employed to provide electrical shielding to the thermocouple leads from the effects of the magnetic field. For the same reason the thermocouple leads were also sheathed with nickel foil. The thermocouples thus arranged were then positioned successively at various depths inside the hot zone of the furnace and temperature measurements were made. These profiles are shown in Figure 3.7. Two power settings were employed, corresponding to maximum temperatures in the hot zone of approximately 1450 °C and 1500 °C, which produced the two different profiles shown in Figure 3.7, which shows variation in temperature with position in the hot zone of the furnace (z) measured from the topmost coil in the assembly. From Figure 3.7 the temperature gradient in the region of the hot zone corresponding to the mushy zone of RR-2100 (120 < z < 150 mm) was then evaluated for the two different power settings. The results are shown in Table 3.2 and were found to be consistent with the results in Ref [62] obtained on the same equipment. The apparatus was re-calibrated due to changes made to the apparatus, a graphite susceptor was used in place of a molybdenum susceptor.
Table 3.2. Temperature gradients in the mushy zone corresponding to the two different power settings.

The gradients thus obtained were found to be consistent in every run. Additionally, the quenching rate was also determined by quenching the thermocouple assembly described above in a water bath and recording the thermal curve on a chart recorder. The quenching rates were determined to be on the order of 450 °C/s. The error in this estimate was considered to be ± 50 °C/s. It is to be mentioned regarding the quenching tests that the response time of the thermocouple was sufficiently small to obtain continuous acquisition of data. It was also observed that during the quench, the thermocouples recorded a constant temperature for a period of about 1s before the temperature started to drop rapidly.

Once the apparatus was characterized the experiments with the RR-2100 samples were conducted. For obtaining results under different cooling rates, three different withdrawal rates were employed, corresponding to 1, 2 and 6 mm/min.

The sample was cleaned with acid and any oxide scale scraped off with a file prior to melting. Once cleaned, the specimen was placed between $z \approx 90$ mm and $z \approx 170$ mm. Since the sample was in single crystal form to start out with, a small unmelted region at the bottom of the sample typically 5 – 10 mm in length (between $z = 160$ and $170$ mm) was employed as a seed to

<table>
<thead>
<tr>
<th>Maximum Temperature in DSQ furnace [°C]</th>
<th>Temperature gradient in the region corresponding to the mushy zone [°C/mm]</th>
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<tbody>
<tr>
<td>1450</td>
<td>~ 6</td>
</tr>
<tr>
<td>1500</td>
<td>~ 10</td>
</tr>
</tbody>
</table>
ensure that the dendrite growth direction in the directionally grown region was close to the <001> orientation.

A typical run would be as follows:

1) The sample is placed inside the crucible and is positioned between \( z = 90 \) and \( z = 170 \) mm.
2) The cold furnace is evacuated and purged with argon gas which is circulated through the system throughout the course of the experiment.
3) The power in the induction coil is switched on.
4) One hour is allowed for the temperature in the furnace to reach a steady state.
5) The sample is lowered through the hot zone at one of the prescribed speeds (1, 2 or 6 mm/min). The samples were lowered through a distance of approximately 26 mm or 1 in. Thus, the withdrawal times were different for the three speeds.
6) Once the sample has traversed this distance, it is quickly quenched in a water bath at the bottom of the DSQ assembly.

After the furnace cooled down, the sample was removed. All samples emerged from the test sufficiently clean without any scale or oxide “skin”. The specimen was then cleaned with acid and the directionally grown region was analyzed for dendrite growth direction with Laue Back reflection.

Following analysis of the Laue back reflection patterns the specimens were cut longitudinally along the dendrite growth and prepared for observation of the microstructure for obtaining visual proof of single crystal structure in addition to the primary dendrite arm spacing. The specimens were polished to a 1 \( \mu m \) finish with diamond paste and etched for approximately 60 s using
a solution of the Pratt and Whitney #17 etch comprising of 50 mL HCl, 50 mL HNO₃, 1.5 g molybdic acid and 75 mL H₂O [104]. This etchant preferentially attacks the γ' and produces good image contrast for optical metallography. The longitudinal sections were observed with a Nikon Epiphot 300 optical microscope.

The primary dendrite arm spacings were measured by measuring the dendrite core-to-dendrite core distance for a number of dendrites in each of the test specimens using the image analysis software Clemex Vision© Version3.5-Professional Edition, calibrated for the Nikon Epiphot 300 optical microscope. These measurements were repeated with transverse sections to verify the validity of the measurements made on the longitudinal sections. The results were found to be similar.

In addition to standard metallographic analysis, specimens were also prepared for Electron Probe Microanalysis (EPMA) [105]. These specimens were polished to a 1 μm finish with diamond paste and coated with graphite for ensuring a path to ground for the electrons. The following section details the EPMA method used for obtaining the chemical composition of the mushy zone, for evidence of microsegregation.

3.4 Electron Probe Microanalysis Experiments

The directionally solidified specimens were cut longitudinally along the dendrite growth direction, and the section thus obtained was prepared for EPMA scans. Figure 3.8 shows a schematic illustration of the EPMA scans made. The equipment used was a Cameca SX-50 electron probe microanalyser. Measurements were made in the mushy zone over a region 50 \( \lambda \times 25 \lambda \) \( \mu m^2 \) at a spacing of 20 μm in the radial direction and every 300 μm
in the longitudinal direction: \( \lambda \) is the primary dendrite arm spacing in the sample. The mushy zone was identified with the knowledge of the freezing range (\( \Delta T_{L\rightarrow S} \)) of the alloy and the temperature gradient (\( G \)) in the specimen. The temperature at the solid liquid interface is the liquidus temperature (\( T_L \)) $1710$ K. Since the freezing range of the alloy was identified by DSC experiments to be about $70$ K (see § 3.2) then the depth ($D$) of the mushy zone is given approximately by $\Delta T_{L\rightarrow S} / G$, measured from the dendrite tips. Additionally, with knowledge of the temperature gradient, the temperature ($T_d$) at any given depth ($d$) in the mushy zone measured from the dendrite tips is given by:

\[
T_d = T_L - dG
\]

Eq. 9

The wavelength dispersive spectrometers (WDS) employed in the microprobe were equipped with crystals of LiF or Lithium Fluoride (for detection of Cr, Co, Ni, and Re peaks), TAP or Thallium Acid Phthalate (for detection of Al, Ta peaks) and PET or Pentaerythritol (for detection of W peaks) [105]. X-ray peaks and backgrounds were recorded simultaneously for Al· Ka, Co· Kα, Cr· Kα, Ta· Mα, W· Mα, Re· Lα and Ni· Kα. The peaks from the sample were compared with the peaks from pure element standards and converted to concentration values using standard correction procedures [105,106]. Table 3.3 shows the parameters used for the scans.

In addition to the scans described above, point scans for the composition both in the dendrite centres and in the interdendritic regions were made for some dendrites, from $X=0$ µm representing the top of the mushy zone or near the dendrite tips, to $X=6000$ µm representing the bottom of the mushy zone. The choice of the dendrites was subject to the criteria that first the dendrites cores must be completely visible from the top of the mushy zone to the bottom
so that measurements could be made in the exact centres and second that there must be at least three such dendrites adjacent to each other so that a meaningful averaged value of composition could be obtained from the scans. The objective was to determine any change in composition from the top of the mushy zone to the bottom, both in the solid and in the interdendritic region. The point scans were made at intervals of every 300 \( \mu \text{m} \). Refer to Figure 3.9 for a schematic illustration of these scans. These scans were repeated with different beam sizes (7, 5, 3 and 1 \( \mu \text{m} \)) for quantifying the effect of beam size on the accuracy of the measurements. The beam size employed for making the measurements is central to the determination of the composition at a particular point. It is expected that larger beam sizes should give more averaged reports of concentration. In order to quantify the reliability of the measurements, a point randomly chosen on a specimen was analyzed using four different beam sizes of 1, 3, 5 and 7 \( \mu \text{m} \). The results are shown in Figure 3.10. It can be seen that the composition differences reported are within the error of the WDS measurement technique, although the measurements of composition of the heavy elements Ta and W were more prone to change. Thus, it can be concluded that the effect of beam size on the measurements should not produce an appreciable variation. The measurement point corresponds to a measurement in the interdendritic region.

It is to be noted that with careful polishing the dendrites were easily discernible by electron backscattered signals without any etch. The dendrites appear bright, being rich in heavy solute elements such as rhenium or tungsten, while the interdendritic regions appear dark as they do not contain appreciable concentrations of these heavy elements.

In the EPMA scans of the longitudinal sections, the chemical analyses recorded all the major and minor elements relevant to the standard
composition of the alloy. However, hafnium present to the extent of 0.15 wt % was not taken into account.

<table>
<thead>
<tr>
<th>Beam Current</th>
<th>Accelerating Voltage</th>
<th>Take-off angle</th>
<th>Counting time</th>
<th>Beam size</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 nA</td>
<td>20kV</td>
<td>40°</td>
<td>63 s</td>
<td>5 μm</td>
</tr>
</tbody>
</table>

Table 3.3. The parameters employed for EPMA scans.

All these experiments were conducted with the ultimate objective of obtaining evidence for back diffusion in the alloy during solidification and developing a model of microsegregation incorporating back diffusion to explain the observed results. For this purpose information from each of individual experiments (DSC, DSQ, optical metallography and EPMA) was used. The following chapter presents the results from these experiments and analysis and discussion can be found therein.
Figure 3.1. Laue Back Reflection pattern of as received RR-2100 sample. Point O is the reflection of the \{001\} plane and thus the dendrite growth direction is a few degrees away from the East-West axis.

Figure 3.2. Schematic illustration of the procedure for quantitative DSC measurements, baseline, calibration and measurement runs.
Figure 3.3. Schematic illustration of the signal obtained from the DSC runs (after [101]).

Figure 3.4 Plot of specific heat vs temperature during solidification for the alloy RR·2100. X = Liquidus, Y = Solidus.
Figure 3.5. Variation of the solid fraction with temperature as determined from the DSC measurements.

Figure 3.6. Schematic illustration of the DSQ furnace.
Figure 3.7. Temperature profile of the DSQ furnace at two different power settings.

Figure 3.8. Schematic illustration of EPMA scan made in the mushy zone of RR-2100 alloy. Longitudinal section shown.
Figure 3.9. Schematic illustration of EPMA point scans in the dendrite centres and interdendritic regions.

Figure 3.10 Bar graph showing the effect of beam size on the measurement of composition.
Chapter 4

Results, Discussion and Analysis
4.1 Introduction

Microsegregation in commercial metal alloy systems has been a topic of active research. These systems are often complex in terms of composition and as a result, understanding the phenomenon of solute redistribution during solidification in these systems suffers from various complications arising from thermodynamic and kinetic effects, and geometry [89-94]. Nevertheless, as was seen in Chapter 2, the predictions of these models agree reasonably well with microsegregation data for ternary and quaternary systems. But experimental data for higher order systems, particularly nickel–base superalloys, are scarce. The aim of this thesis is to obtain experimental proof of back diffusion in nickel–base single crystal superalloys at the scale of the primary dendrites and to arrive at a model of microsegregation to characterize it. In order to achieve this aim, as was reasoned in Chapter 3, there was a need for carefully targeted experiments. This chapter presents the results from these experiments and the subsequent modeling to interpret them.

4.2 Dendrite Morphology

Dendrite arm spacings in directionally solidified components are important microstructural features which determine basic transport phenomena in the mushy zone affecting subsequent mechanical properties of the cast product. The dendrite arm spacings directly influence convection in the mushy zone and determine the occurrence of defects such as freckles, channel segregates and porosity in the microstructure [61]. For the alloy RR-2100 studied herein, the directional solidification experiments have been described in § 3.3. Figure 4.1 shows the microstructures of the longitudinal section of a directionally solidified specimen. The quenched liquid atop the mushy zone is clearly
visible. Since the etchant used (refer to § 3.3) attacks the γ' phase, the interdendritic regions which are rich in γ' forming elements appear darker in contrast to the dendritic solid. The mushy zone etched lightly in comparison to the rest of the specimen. The quenched liquid exhibited equiaxed grains of fine dendrites, in comparison, the dendrites in the mushy zone were rather coarse. Measurements of the dendrite arm spacings for the two different gradients imposed are shown in Figure 4.2. The average primary dendrite arm spacings measured were found to be consistent with observations reported elsewhere in the literature for superalloys solidified under similar conditions [53,61]. (It is to be noted that hereafter the primary dendrite arm spacing will be referred to as the "arm spacing" for convenience.) The dendrite arm spacings in the RR-2100 alloy samples studied were found to be 250, 200 and 120 µm corresponding to withdrawal rates of 1, 2 and 6 mm/min respectively. The single crystal structure of the alloy specimens can be confirmed from Figure 4.1. Proof of of the orientation of the dendrites can be seen in the Laue Back Reflection patterns (see Figure 4.3). The four-fold symmetry can be seen about point O and this was confirmed to be the reflection of the {001} plane. This point is approximately 10° away from the East–West axis which is the <001> direction. Thus the dendrite growth direction is close to the <001> direction. It is to be noted that freckles were not observed in any of the DSQ specimens, as expected due to the relatively small cross-section of the samples (about 20 mm²) consistent with the observations of Auburtin [62].

4.3 EPMA Measurements of Composition

The method of the electron microprobe measurements of composition in the mushy zone were described in § 3.4. A set of point scans made along a horizontal line at any given depth in the mushy zone (see Figure 3.10) would
represent the entire range of solid fractions in the half arm space at that
depth, provided a large number of scans be made. Point scans were made
approximately 20 µm apart along any given horizontal line, with a total
number of scans on the line being about 150 in number. It should be noted
that with a large number of point scans made with EPMA, the statistical
noise in the data is significant [53]. Thus the statistical technique of Gungor
[107] was adapted to help in this situation. This technique was originally
applied to binary alloys to estimate the solidification path and subsequently
the composition of the first solid to form. Based upon an estimate of the solid
composition at the dendrite core, the equilibrium partitioning ratio for the
solute can be calculated as the ratio of the composition at the dendrite core to
the mean composition determined. In this regard it should however be noted
that it has been observed [2] in this class of materials that Re and W have a
high tendency to partition to the dendrite cores, while Al and Ta partition
strongly to the liquid or the interdendritic regions. Other elements such as Co
and Cr, show only a moderate preference for partitioning to the dendrite
cores, their partitioning ratios being only slightly greater than unity [53,67].

In a multi-component alloy such as RR-2100 there are several solute
elements, each partitioning differently. Thus in order to determine the
solidification path the procedure adopted by the authors in Ref [53] was
chosen. Since it is anticipated that Re and Ta segregate strongly in different
directions, the magnitude of the quantity \( (C_{Ta} - C_{Re}) \) is used as a basis for
estimating the solid fraction \( f_s \) to which it corresponds. The procedure
employed [53,107] consists of:

(i) Sorting the datapoints into ascending order on the basis of the local
value of the quantity \( (C_{Ta} - C_{Re}) \)

(ii) The assignment of an integer \( i \) lying between unity and \( N \) on this
basis, where \( N \) is the number of datapoints collected
(iii) The quantity \( f_s \) is placed equal to the ratio given by \( (i-1)/(N-1) \) which is assumed to equate to the fraction solidified at this point.

(iv) The computation of the mean concentration values within appropriately chosen intervals of \( f_s \) (for example 0.02).

Figure 4.4 shows an example of the unsorted data values of concentration for rhenium, in RR-2100 solidified under a temperature gradient of 10 °C/mm and a withdrawal rate of 6mm/min. The plot shows the compositions measured along a horizontal line at a depth of 600 μm. It is not possible to extract any information from this raw data regarding variation of composition with fraction solidified. The sorting algorithm helps in this regard. The concentrations of Re, Al, W and Ta at different depths in the mushy zone as a function of the solid fraction \( f_s \) obtained by the procedure described above are given in Figures 4.5 through 4.8 which show the concentration profiles at four different depths in the mushy zone; the solidification conditions are identical to those stated above. Also shown are the corresponding Scheil and Equilibrium predictions of the solute profiles, made using the software Thermocalc and its database of thermodynamic parameters [70]. From these figures the partitioning ratios of the alloying elements can be estimated from the composition value at the limit of zero \( f_s \). The values determined in this way are reported in Table 4.1. The values for the partitioning coefficients determined therein agree well with values reported elsewhere [53,67,108,109], although it is interesting to note that partitioning coefficients, e.g. of W, are not always reproduced by Thermocalc. The following sub-sections discuss the different aspects of these plots.
4.3.1 Interpretation of the sorted data in terms of a volume element

The data are plotted between the limits of $f_s = 0$ and $f_s = 1$. The sorting method ascribes a value of solid fraction, $f_s$, to a given data point based upon the local value of the quantity $(C_{Ta} - C_{Re})$. The data point reporting a minimum value of this quantity corresponds to $f_s = 0$, and the one reporting a maximum value corresponds to $f_s = 1$. Once the data points are sorted on this basis, the composition can be reported as a function of the solid fraction as shown in Figures 4.5 through 4.8 at different depths in the mushy zone.

<table>
<thead>
<tr>
<th>Element</th>
<th>Partitioning Coefficient ($k$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.78 ± 0.04</td>
</tr>
<tr>
<td>Re</td>
<td>1.66 ± 0.03</td>
</tr>
<tr>
<td>Ta</td>
<td>0.67 ± 0.09</td>
</tr>
<tr>
<td>W</td>
<td>1.47 ± 0.06</td>
</tr>
<tr>
<td>Co</td>
<td>1.09 ± 0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>1.0 ± 0.08</td>
</tr>
</tbody>
</table>

Table 4.1 Equilibrium partitioning coefficients determined for the alloy RR-2100, the value are reported at 1 wt% solid calculated at the liquidus temperature from the sorted EPMA data at a stage corresponding to a solid fraction of zero.

Such a plot can be thought to represent the concentration profile in a volume element in the half-arm space between two dendrites, provided the data collected represent the entire range of solid fractions therein. The length scale of a volume element in the half-arm space is expressed in a normalized form such that $L_s = 0$ corresponds to the dendrite cores and $L_s = 1$ corresponds to the midpoint between two adjacent dendrites. Thus, Figure 4.5a shows the
concentration profile of rhenium in the volume element between two adjacent dendrites at a distance of about 6000 µm from the dendrite tips. Figure 4.5d on the other hand shows the concentration profile of rhenium in the volume element between adjacent dendrites at a distance of about 300 µm from the dendrite tips.

4.3.2 Position of the solid–liquid interface in the volume element

Within the mushy zone of the alloy specimen, the extent to which solidification should have proceeded prior to the quench increases with distance from the dendrite tips. Thus, the position of the solid–liquid interface in terms of the normalized space variable $f_s$ in the volume element increases towards the limit of $f_s = 1$ with distance from the dendrite tips. Thus, in Figures 4.5a, 4.6a, 4.7a and 4.8a showing the concentration profile in a volume element in the half–arm space at the bottom of the mushy zone, solidification should be close to completion and therefore the position of the solid–liquid interface should be close to the limit of $f_s = 1$. On the other hand, in Figures 4.5d, 4.6d, 4.7d and 4.8d, which represent the concentration profile in a volume element at a distance of 300 µm from the dendrite tips, the solid–liquid interface should be found closer to the limit of zero $f_s$. The temperature at any distance from the dendrite tips can be estimated using Eq. 9. With this temperature, the fraction solidified at different depths can be estimated from the $f_s$ vs $T$ curve in Figure 3.5 by interpolation with the method of cubic splines [110,111]. Thus, it was estimated that at a depth of 300 µm, the solid fraction should be about 0.15, corresponding to the position of the solid–liquid interface in the volume element. Thus for example, the sorted data in the domain $0 \leq f_s \leq 0.15$ in Figures 4.5d, 4.6d, 4.7d and 4.8d represent the composition of the solid in the volume element, and the data in
the domain $0.15 \leq f_s \leq 1$ represent the compositions of the interdendritic regions. Similarly, the solid and liquid domains in the normalized half-arm space at different depths can be estimated knowing the position of the solid – liquid interface at the termination of solidification. The positions of the solid–liquid interface at depths of 6000 μm, 4800 μm and 1500 μm were estimated to be 0.99, 0.99 and 0.58 respectively.

### 4.3.3 Scheil and Equilibrium predictions

In Figures 4.5 through 4.8 the corresponding Scheil and lever rule predictions for the solute profile in the volume element are also shown. These calculations were made with the thermodynamic database of the software Thermocalc. The equilibrium calculation assumes that diffusion in both the solid and the liquid phases is complete during solidification. Thus the composition of each phase is uniform and a constant value is reported. In the Scheil calculation however, the liquid concentration changes during solidification. This can be understood by examining Figure 4.9 which shows a schematic illustration of the changing solute profile in a volume element under classical non–equilibrium conditions. As the interface advances the liquid composition in the arm space decreases (for solute with $k>1$) monotonically below the equilibrium limit of $C_0$ with time, for a solute with a partitioning ratio lesser than unity the liquid concentration continuously increases above $C_0$. Thus, as solidification proceeds the solid composition at the interface ($= kC_i$) should decrease continuously for the former and increase for the latter type of solute. The schematic illustration in Figure 4.9 depicts a snapshot of the solute profile at a particular instant in time during Scheil solidification.
Since the RR-2100 alloy sample was quenched in the DSQ run and the solidification conditions were frozen-in, the sorted data at different depths should represent a snapshot of the compositions of the solid and the liquid phases present in the arm space just prior to quenching. Therefore, in order to correctly interpret the sorted data at different depths, the corresponding Scheil and equilibrium lever rule predictions were also truncated at prescribed solid fractions. The termination solid fractions were determined as described in § 4.3.2. For example in Figures 4.5c, 4.6c, 4.7c and 4.8c, the solid-liquid interface is present at a value of $f_s = 0.58$ at the termination of solidification by quenching. Therefore the Scheil and equilibrium predictions were truncated at this value and they predict the concentration profile of the solid in the region corresponding to $0 < f_s < 0.58$. As diffusion in the liquid is assumed to be complete in both the Scheil and the equilibrium analyses, the liquid compositions at the truncation solid fraction value are assumed to be the composition in the entire liquid region of the half-arm space in each of these calculations. Therefore, the composition in the entire liquid domain defined by $0.58 < f_s < 1$ is reported as constant and equal to the composition at the solid-liquid interface.

It is to be noted regarding the Scheil and Lever rule predictions that the eutectic reaction (L $\rightarrow \gamma + \gamma'$) occurs at a solid fraction of about 0.65, evident from the sudden change in solid concentration in Figures 4.5a, 4.6a, 4.7a and 4.8a. Thus after the stage at which the eutectic reaction occurs, the compositions in both Scheil and lever rule predictions are reported as weighted averages of the two phases; it is being assumed that the EPMA method is incapable of resolving differences in composition between the $\gamma$ and $\gamma'$ phases. The reason for this sudden change can be understood as follows. Consider the Scheil prediction in Figure 4.5a: therein, the average rhenium content in the gamma and the gamma prime phases combined is calculated
as the ratio of the total weight of rhenium in the two phases combined to the total weight of the gamma and the gamma prime phases at a given instant in time during solidification. Referring to Figure 4.10 which shows the variation in the predicted amounts of the gamma and gamma prime phases forming in the system as a function of the solid fraction, $f_s$, it can be seen that at $f_s = 0.65$ when the eutectic reaction is predicted to occur, the amount of the gamma phase forming is quite small, however, the weight of the gamma prime phase precipitating out of the system at this stage is comparable in magnitude to the gamma phase. Thus, the denominator in the ratio described above almost doubles after $f_s = 0.65$. Consequently, the ratio is halved, and there occurs a sudden drop in the average composition of the solid.

The trend in the experimental EPMA data however, does not correspond perfectly to either the Scheil or the lever rule predictions although the Scheil predictions are a better fit. It is to be noted in this regard that the prediction Thermocalc for tungsten is rather poor. This is an indication of the inadequacy of the thermodynamic database employed [70]. However, the decreasing trend in composition with solid fraction seen in the sorted data values of tungsten is similar to that observed by the authors in Ref. [53].

### 4.3.4 The question of back diffusion

This deviation from the Scheil and lever rule predictions can be attributed to the effects of solute diffusion which results in a composition profile different from the two limits. At this stage however, it is not clear to what extent back diffusion has a contribution. However, the solute profiles shown reveal a behaviour as expected: Al and Ta partition to the liquid, thus in the half–arm space, the concentrations of Al and Ta increase as we proceed from the dendrite center ($f_s = 0$) to the interdendritic regions ($f_s = 1$). The reverse is
observed in the data for the elements Re and W, which partition to the dendrite cores.

The sorted EPMA data does not reveal a sudden change in the composition at the interface neither does it report a constant liquid composition as predicted by the Scheil and lever rules. This can be attributed to two effects. First, the EPMA scans were made with a beam size of 5 μm. The composition reported in the EPMA measurements is an average value over a small region of interaction of the beam with the sample's surface. Thus when the beam is moved from the dendrite cores to the interdendritic regions gradually, because of this averaging effect, there should not be any sudden changes in composition. Second the solid–liquid interfaces during growth are not planar; secondary arms are readily visible in the optical micrographs. The Scheil and lever rule predictions assume that the interfaces are perfectly planar and side arms are neglected. However, the EPMA scans along horizontal lines contain data for the composition of the secondary arms as well (see Figure 4.11). Therefore the composition should gradually change from the primary dendrite spine through to the outer tips of the secondary arms and finally to the interdendritic liquid in the arm space. The sorting method will therefore not reveal a jump in the concentration profile. Additionally it must be acknowledged that the volume element after sorting can represent any one of the situations shown in Figure 4.11, i.e., it may be above or below the exact center of the secondary arms.

However, the data between $0 \leq f_s \leq f^*$, where $f^*$ corresponds to the position of the planar solid–liquid interface (refer to Figure 4.11) should contain data for the composition of the primary dendrite trunks. Examination of this domain in Figures 4.5 through 4.8 reveals that the trends in the data do not correspond perfectly to either the Scheil or the lever rule predictions, although the Scheil predictions are in closer agreement. At this juncture any
contribution from back diffusion, if at all, is not evident. However, the sorted data in the domain defined by \( f_s^* \leq f_s \leq 1 \) can correspond to any of the three types of regions shown in Figure 4.11 in a volume element in the half-arm space of adjacent dendrites. The concentration profile in this region cannot be estimated from an analysis of the volume element in the primary half-arm space alone; diffusion processes occurring in an orthogonal direction in the secondary arms will have an impact on the concentration profiles in the primary half-arm space. However, the sorted data in the domain \( 0 \leq f_s \leq f_s^* \) can be tested for evidence of back diffusion with a suitable model (see § 4.4).

### 4.3.5 EPMA scans in the dendrite cores and interdendritic regions

At this juncture it is instructive to study the data of the composition of the interdendritic region at different distances from the dendrite tips to note the variation in the liquid composition with depth in the mushy zone.

Figures 4.12 through 4.14 show the data obtained from the EPMA scans made both along the dendrite centres and in the interdendritic regions (refer to Figure 3.9) measured at the mid-point between dendrites in three different specimens. The temperature gradient in the mushy zone was approximately identical in the three samples but different withdrawal speeds were employed; thus the local solidification times were different. As can be seen, there is little variation in the composition at the dendrite centre from the top of the mushy zone to the bottom. However, the compositions of the interdendritic regions show a different trend. For elements such as Re and W, whose partitioning coefficients are greater than unity, the interdendritic liquid composition decreases from a value close to the bulk composition \( C_0 \) of the alloy at the top of the mushy zone, to a minimum value at about 2700 \( \mu \text{m} \) from the dendrite tips, and then increases to a value slightly less than \( C_0 \) at
the bottom of the mushy zone. On the other hand, for elements such as Al and Ta that partition strongly to the interdendritic region, the liquid composition increases from a value close to the bulk composition $C_0$ of the alloy at the top of the mushy zone, to a maximum value again at about 2700 μm from the dendrite tips, and then decreases to a value slightly greater than $C_0$ at the bottom of the mushy zone. The reason for this behaviour observed in the data of composition of the interdendritic regions needs to be rationalized. This is done below.

While making measurements of composition of the interdendritic regions it was observed that it was easier to locate the liquid regions between adjacent dendrites at shorter distances from the dendrite tips. It can be seen from an examination of Figure 4.1 that at the top of the mushy zone the secondary arms of adjacent dendrites do not coalesce and the interdendritic liquid (which is darkly etched) can be located with relative ease. In Figures 4.12 through 4.14 it can be seen that the measured composition of the liquid in these regions ($0 \leq X \leq 2700 \mu m$) decreases for Al and Ta and increases for Re and W with depth in the mushy zone. However, at greater depths ($X > 2700 \mu m$) corresponding to higher solid fractions, the side arms are not distinct and they coalesce. At these depths, the liquid fraction is small. Thus, measurements of the liquid composition at greater depths suffer from the difficulty of locating the liquid. If the EPMA scans were indeed made in the quenched liquid then the trend in the composition should probably be similar in form to the Scheil prediction, there should be a continuous decrease or increase depending on the partitioning coefficient $k$. In other words, for Re and W the liquid composition should decrease monotonically with depth in the mushy zone and the liquid composition of Al and Ta should increase, and there should not occur a reversal in the trend. However, if the interdendritic scans at greater depths in the mushy zone were made at or in the vicinity of
the outer tips of the secondary arms, then the compositions reported should correspond to those of the solid. These will be different from the corresponding liquid compositions at that depth by a factor approximately equal to the magnitude of the partitioning coefficient $k$, and this will result in the reversal observed in the data in Figures 4.12 through 4.14. Therefore it can be concluded that the measurements of the composition of the interdendritic regions at greater depths are influenced by the compositions of the solid. At this juncture however, it is still not clear whether back diffusion has any contribution or not, which would serve to change the liquid composition profile away from the Scheil and toward the equilibrium limit.

Figure 4.15 shows the comparison between the data from the scans along horizontal lines and the composition of interdendritic region measured at the mid-points between dendrites. The square markers represent the data from Figure 4.10 while the round markers represent the weighted average of the composition calculated from the EPMA data in Figures 4.5 through 4.8. Lines are also drawn through the data, as a guide to the eye. With regards to calculating the weighted averages of the composition of the interdendritic regions from Figures 4.5 through 4.8 it is to be noted that the EPMA point scans carried out in the interdendritic regions were subject to human error in locating the exact mid-point between two adjacent dendrites; the precision in locating this region was considered to be $\pm 10 \, \mu m$, thus, the weighted averages of composition were calculated over a region between the mid-point of two dendrites ($f_s = 1$) and a region in the arm space $10 \, \mu m$ away from this point ($f_s = 0.83$). Thus the weighted averages for composition in the domain defined by $0.83 \leq f_s \leq 1$ were calculated using the relationship:
\[
\int_{0.83}^1 C_i(f_s) df_s \\
\frac{\int_{0.83}^1 df_s}{0.83}
\]

where \( i \) refers to one of the four solutes Al, Re, W or Ta.

It can be seen from Figure 4.15 that the averages calculated in this way agree well with the measured values of composition of the interdendritic regions at different distances from the dendrite tips. Since it was concluded that the EPMA scans made in the interdendritic regions at distances greater than approximately 3000 \( \mu m \) from the dendrite tips were measurements of solid composition in the secondary arms rather than the liquid, the comparison in Figure 4.15 confirms that the EPMA data obtained from the horizontal scans contain information of the composition of the secondary arms near the limit of \( f_s = 1 \).

From the preceding discussion the following points emerge:

1) The sorted EPMA data for composition reveals that the four elements Re, Ta, W and Al behave as expected in terms of their partitioning, with Re and W segregating to the dendrite cores and Al and Ta segregating to the liquid.

2) The sorted data represent a snapshot of the solidification conditions just prior to quenching in the half-arm space within the mushy zone, representing the solute profile therein including the secondary arms.

3) The partitioning coefficients of the four elements were determined from the sorted data and agree well with values reported in the literature (see Table 4.1)

4) Neither the Scheil nor the lever rule predictions made with Thermocalc agree perfectly with the trends in the data (Figures 4.5 through 4.8).
This is an indication that the there are effects occurring that are not accounted for by these simple models.

5) The composition of the interdendritic region in the mushy zone changes with depth into the mushy zone measured from the dendrite tips, exhibiting a maxima or a minima at a certain depth depending on the partitioning ratio of the solute in question. This is an artifact from the EPMA measurement method and does not explain whether or not back diffusion in the solid changes the liquid concentration prior to the maxima or minima observed.

6) There is a need to explain the trends observed in the data with a suitable model, which must be able to predict the solid as well as the interdendritic liquid composition.

The following section describes the model used to correctly interpret the physical conditions to which the data correspond.

4.4 Modelling the Microsegregation in RR-2100

Examination of the data of composition from the EPMA experiments does not reveal whether or not there is significant back diffusion during solidification. The DSC experiments however, suggest that the solidification path of the alloy RR-2100 lies between the limits of the Scheil and lever rules, thereby implying that back diffusion is indeed occurring. A model for microsegregation has been developed to predict with reasonable accuracy the solidification path as observed in Figures 4.5 through 4.8.

The approach taken in this study to model the solute segregation is based upon the familiar method of conservation of solute in the half-arm space. As
with all models, some simplifying assumptions are necessary in order to be able to treat the system from a mathematical standpoint.

Stated below are the governing assumptions central to the derivation:

1) The primary dendrites are taken to have a plate-like morphology.
2) The solidification front is assumed to be perfectly planar and lies perpendicular to the growth direction and the presence of side arms is neglected.
3) There is negligible undercooling before nucleation, or from curvature or kinetic effects.
4) The system is considered to be closed, thus there is no mass flow in or out of the control volume.
5) The liquid phase is considered to have a uniform composition; diffusion is considered to be complete, thus composition gradients are eliminated during solidification.
6) The equilibrium partitioning ratio, \( k \), is assumed to be constant throughout solidification.
7) Diffusion within the solid phase occurs by volume diffusion, governed by the diffusion coefficient \( D_s \), which is a function of temperature.
8) The average composition in the half-arm space remains fixed at the initial value of \( C_0 \), or in other words there is no macrosegregation.
9) At any instant in time, the temperature in the half-arm space is assumed to be uniform at any given distance from the dendrite tips, or in other words heat diffusion is assumed to be rapid and complete.

Consider a volume element in the half-arm space as shown in Figure 2.8. It follows from assumptions (4) and (8) that the solute balance in the half-arm space can be written as:
\[
\int_0^x C_s \, dx + (X_0 - x_s)C_i = X_0 C_0
\]

Eq. 11

where \( x_s \) is the length of the solid phase in the half-arm space, and \( X_0 \) the total length of the volume element and \( C_s, C_i, C_0 \) are the solid, liquid & bulk compositions respectively.

Modifying Voller's approach [112] for deriving the governing equation for the solute balance in the half-arm space, the space and time variables are normalized as:

\[
\eta = \frac{x}{X_f}, \quad \tau = \frac{t}{t_f}
\]

Eq. 12

where \( x \) and \( t \) are the space and time variables respectively, and \( X_f \) and \( t_f \) are the final values at the end of solidification. Thus Eq. 11 can be written in terms of the dimensionless space and time variables:

\[
\int_0^\eta C_s \, d\eta + (\eta_0 - \eta_s)C_i = \eta_0 C_0
\]

Eq. 13

Progress is made by differentiating Eq. 13 with respect to \( \tau \), the normalized time variable:

\[
\frac{\eta}{\partial \tau} \frac{\partial C_s}{\partial \eta} d\eta + \int_0^\eta d(C_s \frac{d\eta}{d\tau} + (\eta_0 - \eta_s)\frac{dC_i}{d\tau} - C_i \frac{d\eta_s}{d\tau} = 0
\]

Eq. 14

Since we are considering the primary half-arm space, its dimension remains constant during solidification and does not change with distance from the
dendrite tips [113,114], i.e., no coarsening occurs. Thus \( \eta_0 \) is a constant and as a result the RHS in Eq. 14 is zero. After rearranging we obtain:

\[
\int_0^\eta \frac{\partial C_i}{\partial \tau} d\eta + (k-1)C_i \frac{d\eta_i}{d\tau} + (\eta_0 - \eta_s) \frac{dC_i}{d\tau} = 0
\]

Eq. 15

where \( k \) is the partitioning coefficient of the solute.

It is to be noted at this juncture that the solidification domain, i.e., the half-arm space, is defined by \( 0 \leq \eta \leq \eta_0 \). Within the solid domain, \( 0 \leq \eta \leq \eta_s \), solute diffusion is governed by Fick's second law (assumption (7)), thus:

\[
\frac{\partial C_s}{\partial \tau} = \alpha \frac{\partial^2 C_s}{\partial \eta^2}
\]

Eq. 16

where \( \alpha = \frac{\bar{D}_s t_f}{X_f^2} \)

Eq. 17

is the Fourier number for the solute in the solid. \( \bar{D}_s \) is the mass diffusivity of the solute in the solid which depends on temperature. Substituting Eq. 14 in Eq. 13 gives:

\[
\int_0^\eta \frac{\partial^2 C_s}{\partial \eta^2} d\eta + (k-1)C_i \frac{d\eta_i}{d\tau} + (\eta_0 - \eta_s) \frac{dC_i}{d\tau} = 0
\]

Eq. 18

expanding the integral we get:

\[
\alpha \frac{\partial C_s}{\partial \eta} \bigg|_{\eta_i} - (k-1)C_i \frac{d\eta_i}{d\tau} + (\eta_0 - \eta_s) \frac{dC_i}{d\tau} = 0
\]

Eq. 19
Eq. 19 is the governing solute balance equation. The first term on the LHS is an expression of the back diffusion of solute in the solid phase and the second and third terms describe redistribution of the solute in half-arm space due to movement of the solid–liquid interface. A rearrangement of Eq. 19 gives:

\[
\frac{d\eta_s}{d\tau} = \frac{\alpha \frac{\partial C_s}{\partial \eta} \bigg|_{\eta_s} + (\eta_o - \eta_s) \frac{dC_i}{d\tau}}{(1-k)C_i}
\]

Eq. 20

Eq. 20 describes the evolution of the solid fraction with time. This is an ordinary differential equation and is easily treatable with an Euler time marching scheme [112].

This scheme, however, requires the rate of change of the liquid concentration with time to be determined according to:

\[
\frac{dC_i}{d\tau} = \frac{dC_i}{df_s} \cdot \frac{df_s}{dT} \cdot \frac{dT}{d\tau}
\]

Eq. 21

In the alloy RR-2100 the back diffusion parameter \( \alpha \) is small (see later) so that it is assumed that the liquid composition in the arm space is close to the Scheil limit [69]. The rate of change of the liquid composition with solid fraction can be estimated from Eq. 3. The second term on the RHS describes the rate of change of the solid fraction with temperature; this is evaluated by computing the slope of the curve shown in Figure 3.7 at a given value of the solid fraction. The third term on the RHS is the cooling rate employed in the DSQ experiment. Thus,

\[
\frac{dT}{d\tau} = G \cdot V \cdot t_f
\]

Eq. 22
where $G$ is the temperature gradient in the mushy zone and $V$ the withdrawal speed and $t_f$ is the local solidification time.

The rate of change of liquid composition with fraction solidified is given by [64]:

$$\frac{dC_l}{df} = (1-k)C_0 (1-f)^{k-2}$$  \hspace{1cm} \text{Eq. 23}

where $C_0$ is the initial composition.

Within the mushy zone the temperature at any given distance from the dendrite tips ($T_d$) is given by Eq. 9. Thus, the solid fraction is known and the second term is evaluated at $T_d$ at a given distance.

Thus the rate of change of liquid composition can be determined as:

$$\frac{dC_l}{df} = (1-k)C_0 (1-f)^{k-2} \cdot \frac{df}{dT} \cdot G \cdot V \cdot t_f$$  \hspace{1cm} \text{Eq. 24}

Since the local solidification time is given by:

$$t_f = \frac{\Delta T_{L\rightarrow S}}{G \cdot V}$$  \hspace{1cm} \text{Eq. 25}

where $\Delta T_{L\rightarrow S} = T_L - T_S$ is the freezing range of the alloy, combining Eqs. 24 and 25 we get:

$$\frac{dC_l}{d\tau} = (1-k)C_0 (1-f)^{k-2} \cdot \frac{df}{dT} \cdot \Delta T_{L\rightarrow S}$$  \hspace{1cm} \text{Eq. 26a}
The end liquid composition $C_{\text{quench}}$ varies with distance from the dendrite tips and defines the liquid composition at which solidification is terminated by quenching. This can be evaluated at the solidification termination point as:

$$C_{\text{quench}} = C_0 + \frac{dC_i}{d\tau} \cdot n \cdot \Delta \tau$$  \hspace{1cm} \text{Eq. 26b}$$

where $n$ is the number of time step iterations performed till the termination solidification point is reached, and $\Delta \tau$ is the time step size. The derivative in Eq. 26b is evaluated at the termination solid fraction.

An Euler treatment after combining Eqs. 20 and 26 gives:

$$\eta_s = \eta_s^{\text{old}} + \Delta \tau \left[ \frac{B D^{\text{old}} + (\eta_0 - \eta_s^{\text{old}}) \cdot \frac{dC_i}{d\tau}}{(1 - k)C_i} \right]$$  \hspace{1cm} \text{Eq. 27}$$

where $B D = \alpha \frac{\partial C_s}{\partial \eta}$.

It is to be noted that the liquid composition at any point in time is also given by Eq. 26b. The superscript $\text{old}$ refers to values at the previous time step, and the term $B D$ is an approximation for the back diffusion term (see later) in Eq. 20. In each time step the liquid composition is updated based upon the rate of change of liquid concentration with time (Eq. 26). This scheme is solved iteratively and the values of the different variables in Eq. 27 are updated at the end of each time step.

The back diffusion term $B D$ is evaluated within each time step, and the value used during the next time step. This requires the calculation of the solute profile within the solid domain defined by $0 \leq \eta \leq \eta_s(\tau)$. This domain,
however, is changing with time thus the boundary \((\eta_s)\) is moving as well. Therefore, the front is fixed in space using a Landau transformation [115]. Use of a parameter \(\xi\) defined as:

\[
\xi = \frac{\eta}{\eta_s(\tau)} \tag{Eq. 28}
\]

fixes the solid–liquid interface at \(\xi = 1\) for all \(\tau\). The parabolic form of Eq. 16 is amenable to this transformation using the standard relationships:

\[
\frac{\partial C_s}{\partial \eta} = \frac{1}{\eta_s(\tau)} \frac{\partial C_s}{\partial \xi} \tag{Eq. 29a}
\]

\[
\frac{\partial^2 C_s}{\partial \eta^2} = \frac{1}{\{\eta_s(\tau)\}^2} \frac{\partial^2 C_s}{\partial \xi^2} \tag{Eq. 29b}
\]

\[
\frac{\partial \xi}{\partial \tau} = \frac{\eta}{\{\eta_s(\tau)\}^2} \frac{d \eta_s}{d \tau} \tag{Eq. 29c}
\]

\[
\left. \frac{\partial C_s}{\partial \tau} \right|_\eta = \frac{\partial C_s}{\partial \xi} \frac{d \xi}{d \tau} + \left( \frac{\partial C_s}{\partial \tau} \right)_\xi = \frac{\eta}{\eta_s(\tau)} \frac{d \eta_s}{d \tau} + \left( \frac{\partial C_s}{\partial \tau} \right)_\xi \tag{Eq. 29d}
\]

Thus we get:

\[
\left( \frac{\partial C_s}{\partial \tau} \right)_\xi = \alpha \cdot \frac{\partial^2 C_s}{\partial \eta^2} + \left[ \frac{\eta}{\eta_s(\tau)} \frac{d \eta_s}{d \tau} \right] \frac{\partial C_s}{\partial \eta} \tag{Eq. 30}
\]

which describes the changing solute concentration in the solid with time. The solid domain defined by \(0 \leq \xi \leq 1\) remains fixed in time. Eq. 30 is subject to the boundary conditions [112]
\[
\frac{\partial C_s}{\partial \eta} \bigg|_{\eta=0} = 0, \text{ and } C_s\big|_{\eta=\eta_i} = kC_i(\tau)
\]  
Eq. 31

and the initial condition that

\[C = C_0\]

Eq. 32

It is to be noted that the time derivative on the LHS of Eq. 30 is evaluated at constant values of the transformed variable \( \xi \), and the bracketed term on the RHS is the velocity of a constant \( \xi \) point in real space \( \eta \). Eq. 30 can be rearranged as:

\[
\frac{1}{\eta_s} \frac{\partial(\eta_s C_s)}{\partial \tau} = \frac{\partial^2 C_s}{\partial \eta^2} + \frac{\partial}{\partial \eta}\left( C_s \frac{d \eta_s}{d \tau} \right) \]

Eq. 33

The solid domain is divided into a uniform grid of \( m \) nodes, and a time implicit central difference scheme leads to the following formulation at any node \( i \) within the grid:

\[
\frac{C_i \Delta \eta - C_i^{old} \Delta \eta^{old}}{\Delta \tau \cdot \Delta \eta} = \alpha \frac{C_{i-1} - 2C_i + C_{i+1}}{\Delta \eta^2} + \frac{V_{i-1} C_{i-1} - V_{i+1} C_i}{\Delta \eta}
\]

Eq. 34

The values on either side of the \( i^{th} \) node are at points midway between the nodes. \( \Delta \tau \) is the time step size and \( \Delta \eta \) is the grid spacing. \( V_{i-1} \) and \( V_{i+1} \) refer to the velocities of the control volume interface on either side of the node point \( i \), they are defined as:

\[V_{i-1} = \frac{\eta_{i-1}}{\eta_s} \frac{d \eta_s}{d \tau} \text{ and } V_{i+1} = \frac{\eta_{i+1}}{\eta_s} \frac{d \eta_s}{d \tau}\]

Eq. 35
The velocity of the solid–liquid interface is approximated as:

\[
\frac{d\eta_i}{d\tau} = \frac{\eta_i - \eta_i^{\text{old}}}{\Delta \tau}
\]

Eq. 36

where \(\text{old}\) refers to the value at the previous time step. Upwinding [116,117] is used to treat the advection term in Eq. 33. A half cell is assumed at the first node and thus, Eq. 34 for the first node can be written as:

\[
\frac{C_i\Delta \eta - C_i^{\text{old}} \Delta \eta_i^{\text{old}}}{2\Delta \tau \cdot \Delta \eta} = \alpha \frac{C_{i-1} - C_i}{\Delta \eta^2} + \frac{V_{i-1}C_{i-1}}{\Delta \eta}
\]

Eq. 37

Finally, the finite difference equations are closed at the solid–liquid interface boundary (m\(^{\text{th}}\) node) upon noting that \(C_m = kC_i\). A rearrangement of Eq. 34 gives:

\[
C_i \left\{ 1 + \frac{2\alpha \Delta \tau}{\Delta \eta^2} + \frac{V_{i+1}\Delta \tau}{\Delta \eta} \right\} - C_{i-1} \left\{ \frac{\alpha \Delta \tau}{\Delta \eta^2} \right\} - C_{i-1} \left\{ \frac{\alpha \Delta \tau}{\Delta \eta^2} + \frac{V_{i-1}\Delta \tau}{\Delta \eta} \right\} = \frac{C_i^{\text{old}} \Delta \eta_i^{\text{old}}}{\Delta \tau \cdot \Delta \eta}
\]

Eq. 38

The three variables \(C_i\), \(C_{i-1}\) and \(C_{i+1}\) can then be solved for using a tridiagonal matrix algorithm. Once the nodal values are computed, the back diffusion term \(BD\), can be trivially computed using a second order difference formula [115] as:

\[
BD = \left. \frac{\partial C_i}{\partial \eta} \right|_{\eta=\eta_i} = \alpha \frac{3C_m - 4C_{m-1} + C_{m-2}}{2\Delta \eta}
\]

Eq. 39

The partitioning coefficients obtained in Table 4.1 were used in the model. The data for diffusivity for the four elements segregating most, namely, Al, Re, Ta and W were found in the literature and are given in Table 4.2.
Table 4.2 Diffusion coefficients and activation energies for diffusion of Al, Ta, Re and W in the gamma phase, from different sources.

<table>
<thead>
<tr>
<th>Element</th>
<th>$D_0$ [m$^2$/s]</th>
<th>$Q$ [kJ/mol]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>$7.7 \times 10^{-3}$</td>
<td>342</td>
<td>[118]</td>
</tr>
<tr>
<td>Ta</td>
<td>$2.19 \times 10^{-5}$</td>
<td>251</td>
<td>[2]</td>
</tr>
<tr>
<td>Re</td>
<td>$8.2 \times 10^{-7}$</td>
<td>255</td>
<td>[2]</td>
</tr>
<tr>
<td>W</td>
<td>$8.0 \times 10^{-6}$</td>
<td>264</td>
<td>[2]</td>
</tr>
</tbody>
</table>

The model also requires the calculation of the Fourier numbers for the different solutes in the solid, which were calculated using Eq. 17. The local solidification time required for estimating the Fourier number for the RR-2100 sample solidified under a temperature gradient of 10 °C/mm and a withdrawal rate of 6mm/min was computed using Eq. 25 and was found to have a value of 77 s. The values calculated thus, are shown in Table 4.3, which shows the Fourier numbers for the four solutes Al, W, Re and Ta calculated at a temperature of 1660 K, approximately in the middle of the mushy zone.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fourier Number in the solid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>$2.85 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ta</td>
<td>$5.92 \times 10^{-3}$</td>
</tr>
<tr>
<td>Re</td>
<td>$1.66 \times 10^{-4}$</td>
</tr>
<tr>
<td>W</td>
<td>$8.43 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Table 4.3 Fourier numbers of the solutes Al, Ta, Re and W in the solid.

The Clyne & Kurz parameter $\beta$ was evaluated using Eq. 6, and the value was then used to replace $\alpha$ in Eq. 33 for computing the back diffusion in the solid.
Dividing the solid domain into a grid with \( m = 50 \) nodes yielded reasonable convergence. The time step was kept small to reduce numerical errors. In order to obtain solute profiles in the solid in the mushy zone at different distances from the dendrite tips, the solidification was terminated at prescribed values of the solid fraction corresponding to the value at a particular distance from the dendrite tips (see § 4.3). At this stage the composition of the liquid at the solid–liquid interface is \( C_{\text{quench}} \). This analysis was carried out for each of the four elements Al, Re, W and Ta at different distances from the dendrite tips. In a multi-component alloy the front velocities for the different components will be different, thus the front velocity for the slowest diffusing solute was considered to be the limiting velocity, which in RR-2100 is Re; thus the front velocities of the other elements were fixed at the value determined for rhenium. Thus

\[
\frac{d\eta_i'}{d\tau} = \frac{d\eta_{\text{Re}}}{d\tau}
\]

where \( i \) is any solute other than rhenium.

The model described above reduces to the Scheil and Lever rules under limiting conditions, when \( \alpha = 0 \) and \( \infty \) respectively. When \( \alpha \) has values intermediate between the two limits the model gives predictions of the solute profiles in the solid in the half–arm space just prior to quenching. It does not, however, predict the solute profile in the interdendritic region observed in Figures 4.5 through 4.8 which includes the side arms. Like other models of microsegregation, it assumes that the interface between the solid and the liquid phases is perfectly planar, therefore shape instabilities are absent at the interface. The growth of secondary arms occurs after such an instability has set in at the interface (see Figure 4.11 for a schematic illustration), therefore the model cannot describe the concentration profile in the
secondary arms. Once secondary arms start to form, solute diffusion occurs in
the primary as well as the secondary arm space. The model described above
considers diffusion only in one dimension, i.e., in the primary arm space.
Diffusive transport is assumed to occur along the horizontal line shown in
Figure 4.11. Such an analysis cannot account for diffusion in the secondary
arm space which determines the concentration profile in the secondary arms
altering the concentration at the spine of the secondary dendrite arm. In
order to be able to account for this it will be necessary to model the growth of
the dendrite side arms resulting from shape instabilities at the solid–liquid
interface modeling the solute transport in two dimensions accounting for the
changing concentration of the solid and the liquid phases in both the primary
and the secondary dendrite arm spaces. Such an approach would require the
formulation of a suitable finite element mesh mimicking the geometry of the
dendrites with careful attention to the boundary and initial conditions. Such
a detailed analysis is outside the scope of the current study. Figure 4.16
shows a flowchart of the calculation procedures of the model.

4.5 Model Results

Model simulations were run to predict the composition of the solid in the
half–arm space at different distances from the dendrite tips, for each of the
four elements Al, W, Re and Ta. Table 4.4 summarizes the solidification input
parameters used for the model. The values of the partitioning coefficients and
the diffusivities that were employed for the four solutes Re, Al, W and Ta are
given in Tables 4.1 and 4.2 respectively. It should be noted that the
partitioning coefficients used were those determined from the experimental
data presented earlier.
The results are shown in Figures 4.17 through 4.20 which show the variation in solid composition in the half-arm space of the primary dendrite arms for the solutes Re, Al, W and Ta. It is important to remember that the model assumes that the interdendritic region consists only of the liquid phase, and the presence of secondary arms and solute redistribution therein are not considered. Therefore beyond the solid–liquid interface, the model reports that the composition is uniform and equal to the composition of the of the liquid at the solid–liquid interface considering the liquid phase to be solutally well mixed by virtue of diffusion.

It can be seen that the predictions of the model for the solid composition in the domain defined by $0 \leq f_s \leq f_s^*$ corresponding to the primary arms, agree well with the data. In particular, there is complete agreement with the data obtained at the bottom of the mushy zone ($X \approx 6000 \mu m$), at this distance from the dendrite tips, the fraction solidified is about 0.998, or in other words there is no liquid present and solidification is complete. At lower solid fractions, although the agreement is not perfect, one can see that the model is able to account for the composition gradients observed in the solid in the primary arms in a reasonable way. It was discussed previously that the DSC experiments indicated that back diffusion in the solid was occurring during
solidification, but it was not possible to tell whether there was any evidence for back diffusion in the EPMA data of composition in the mushy zone. The model of microsegregation however takes into account back diffusion and produces a reasonable fit to the data. Additionally, the agreement of the model's predictions with the data also validates the sorting algorithm's applicability to reproduce the solidification path in the primary arms. The model developed has better capability in predicting the solidification behaviour than the Scheil and lever rules. This can be confirmed by comparing Figures 4.5a and 4.17a for Re, Figures 4.6a and 4.18a for Al, Figures 4.7a and 4.19a for W and Figures 4.8a and Figure 4.20a for Ta. It should be noted however, that some part of the better fit claimed for the model, e.g. for W, is because more suitable partitioning coefficients have been employed.

Since the data and the corresponding fit produced by the model represent the composition in the half-arm, these data can be mirrored laterally about \( f_s = 1 \) to produce a snapshot of the concentration contours in the entire primary dendrite arm space just prior to the quench. The mirrored data were then used to plot the concentration contours in the mushy zone. Figure 4.21 shows the concentration contours of the four elements Al, Re, W and Ta, after mirroring the data at all the different distances from dendrite tips at which EPMA measurements were made. Also shown are the concentration contours predicted by the model. The sorted EPMA data has been smoothed with a mild Savitzky–Golay filter [119] in order to produce smoother contours so that the plot may be more readable. The blue regions represent areas of low concentration, while the red regions are those corresponding to high concentration. It is to be noted that the scales of the X- and Y-axes are dissimilar. It can be seen by comparing the contours predicted by the model with the data from the EPMA experiments that the agreement is good. The interdendritic regions in the alloy specimen contain secondary arms. Thus,
EPMA information of the composition of the interdendritic regions at various depths contain information for the composition of the secondary arms in Figures 4.21a, 4.21c, 4.21e and 4.21g. The model, however, does not consider secondary arms and assumes that the interdendritic region consists only of the liquid phase. It therefore reports a uniform liquid composition therein. These regions of uniform composition can be seen in Figures 4.21b, 4.21d, 4.21f and 4.21h. However, by comparing Figures 4.21a and 4.21b for Re, Figures 4.21c and 4.21d for Al, Figures 4.21e and 4.21f for W and Figures 4.21g and 4.21h for Ta that the model predictions for the composition of the solid in the primary dendrite trunks are almost identical to the data from the EPMA experiments.

Given this agreement with the EPMA data it can be concluded that since the model considers back diffusion of the solute in the solid phase, it delineates the physical processes occurring during the solidification of the alloy. This shows that the contours of concentration obtained from the EPMA data in Figure 4.21 are the result of back diffusion.

### 4.5.1 Evidence of back diffusion in RR-2100 superalloy

Back diffusion in the solid serves to iron out concentration gradients set up therein during solidification from the partitioning of solute between the solid and the liquid phases. Thus, with increasing solid fraction (or alternatively with greater depth) in the mushy zone the average solute concentration in the solid must approach the equilibrium limit, given sufficient time for diffusion. This is due to the homogenizing effect of back diffusion. If the diffusion parameter $\alpha$ is large or alternatively if the time allowed for solidification is greater, then the diffusion in the solid phase should be closer to completion. Under such conditions the average solid composition should be closer to the equilibrium limit. In the mushy zone of RR-2100, the time
allowed for diffusion to occur in the solid increases with depth. Thus, at greater depths the average solid composition should deviate away from the Scheil and approach the equilibrium limit while it is expected that at lesser depths this value should be closer to the Scheil limit due to the shorter times allowed for diffusion processes to occur.

Figure 4.22 shows the average composition of the solid in the primary arms as a function of depth in the mushy zone, calculated using Eq. 10, for Al, Re, W and Ta. The upper and lower limits of the integration being 0 and $f_s^*$ respectively, where $f_s^*$ is the position of the planar solid-liquid interface in the volume element in the primary half-arm space (see Figure 4.11). The corresponding Scheil and lever rule predictions are also shown calculated from the model in the limits of $\alpha \to 0$ and $\infty$ respectively. The solid lines are the predictions of the model of microsegregation.

The homogenizing effect of back diffusion is readily discernible in these plots. At greater depths in the mushy zone where the time allowed for diffusion is a significant fraction of the local solidification time, the average composition of the solid in the arm space approaches a uniform value deviating away from the Scheil limit. At shorter distances from the dendrite tips however, the average values are closer to the Scheil limit. At greater depths diffusion should have occurred to a larger extent and the concentration gradients set up in the solid by partitioning should be less pronounced. This results in a more uniform solid composition. The effect of back diffusion is thus to redistribute the solute in the already formed solid changing the average solid composition. It can be seen in these plots that the average solid concentration deviates significantly away from the Scheil towards the equilibrium limit beyond a depth of about 3000 $\mu$m in the mushy zone. It can also be seen that both the EPMA data and the predictions of the model lie between the upper
and lower bounds of the lever and Scheil rules. This observation indicates that diffusion in the solid phase during solidification has a specific value.

If the amount of back diffusion was exactly zero then the average composition of the solid should vary according to the Scheil prediction, on the other hand if equilibrium conditions prevailed during solidification then the trends should correspond to the lever rule predictions. However, it is seen that the EPMA data points and the model predictions lie between the two limits clearly indicating the effect of back diffusion. It can also be seen that the model predictions agree almost perfectly with the weighted averages calculated from the EPMA data.

In the plots in Figure 4.22, the composition of the first solid that forms at the tip of the dendrites is determined by the magnitude of the partition coefficient, therefore the average value of the solid composition at the dendrite tips is reported as equal to the product of the partitioning coefficient and the bulk composition of the alloy \((=kC_0)\). Thereafter, the average composition of the solute in the solid either increases (Al, Ta) or decreases (Re, W) from this value to a relatively uniform composition close to the bulk composition of the alloy beyond a depth of about 3000 \(\mu\)m. At this stage the solid fraction in the half-arm space is about 0.9, or in other words, solidification is almost complete, and the effect of back diffusion is to nearly homogenize the solid in the arm space.

If the local solidification time were greater then diffusion should be closer to completion at shorter distances from the dendrite tips and the average composition of the solid in the arm space should approach uniformity. Increasing the local solidification time increases the magnitude of the back diffusion parameter \(\alpha\) and should shift the composition values away from the Scheil and towards the equilibrium limit at shorter distances from the
dendrite tips in Figure 4.22. This increase in diffusion time should result in a complementary effect on the composition of the liquid in the arm space as well. Evidence for the latter however, is not completely clear from the scans made in the interdendritic regions alone (see Figure 4.12) because of difficulty in locating the liquid. However, comparing the data for Re in Figure 4.22a with Figure 4.12a, for Al in Figure 4.22b with Figure 4.12b, for W in Figure 4.22c with Figure 4.12c, for Ta in Figure 4.22d with Figure 4.12d, we see that they are similar at depths exceeding about 3000 μm. The data in Figure 4.22 pertain to the composition of the solid, therefore it can be inferred that the above mentioned agreement between the data in Figures 4.22 and 4.12 gives additional indication that the measurements in Figure 4.12 through 4.14 are measurements in the solid rather than the interdendritic liquid. It is also to be mentioned in this regard that at depths greater than about 3000 μm from the dendrite tips measurements of composition of the interdendritic region might contain information regarding the eutectic reaction. The γ/γ' eutectic nodules should typically be rich in γ’ forming elements, namely Al and Ta and likewise depleted in γ forming elements such as Re and W. These eutectic nodules typically form in between the side arms of adjacent dendrites (the last liquid to solidify), or in other words EPMA point scans in the interdendritic region should detect the eutectic if it forms in any appreciable amount at the end of solidification. It is expected that scans made therein should typically report low concentrations of Re and W (appreciably lesser than $C_o$) and high concentrations of Al and Ta (appreciably greater than $C_o$), but this is not seen in Figures 4.12 through 4.14: the values reported are close to the respective bulk compositions. The reversal in the trends of interdendritic composition resulting in compositions close to the bulk compositions seen in Figure 4.12 through 4.14 can only occur if the measurements beyond about 3000 μm corresponded to the solid composition. Figure 4.23 shows the expected variation in the liquid
composition with depth for the four elements Al, Re, W & Ta according to the Scheil rule as well as according to the model for microsegregation. It can be seen that the Scheil rule and the model both predict a monotonic increase (for Al & Ta) or decrease (for Re & W) in the liquid composition and no reversal is seen. Figure 4.24 shows an optical micrograph of the transverse section at a depth of about 6000 µm in the mushy zone of one of the RR-2100 specimens used in this study. This depth corresponds to the bottom of the mushy zone and therefore should typically contain the eutectic. However the eutectic nodules referred to above were not seen in any of the cross sections examined.

In summary, Figure 4.22 confirms the presence of the phenomenon of back diffusion in RR-2100 superalloy during solidification. It shows that the average solid composition lies between the limits of the Scheil and lever rules, and depicts the homogenizing effect of back diffusion.

4.5.2 Model predictions for different values of parameters $\alpha$ and $k$

The predictions of the model described in the previous sections are for a particular value of $\alpha$, the Fourier number, and a given value of the partitioning coefficient, $k$, as determined from the EPMA experiments. Figure 4.25 shows the predictions of the model for different values of the parameter $\alpha$. The plots show the predictions of the model for the concentration profiles of Al, Re, W & Ta in the volume element at the bottom of the mushy zone for $0 \leq \alpha \leq 10$. At this depth solidification is complete. It can be seen that the model behaves well over a range of values of $\alpha$. In the limit of $\alpha \to 0$ and $\alpha \to \infty$ the model reduces to the Scheil and lever rules respectively and the predictions for intermediate values lie between these two limits. The Clyne–Kurz approximation employed in the model ensured that the back diffusion model functioned well at large values of $\alpha$. The values of the partitioning coefficients used in the predictions in Figure 4.25 are
available in Table 4.1. Figure 4.26 shows the predictions of the model for different values of the partitioning coefficient for the four element Al, Re, W and Ta. The Fourier numbers used are given in Table 4.3. The plots show predictions for 5 different values of $k$. It can be seen that as the value of $k$ deviates from unity the degree of microsegregation increases.

**4.5.3 Interpretation of $\alpha$ and $k$ in terms of fitting parameters**

Although the model predictions in Figures 4.17 through 4.20 seem to produce reasonably good fits to the experimental data it must however be acknowledged that the role played by $\alpha$ and $k$ are those of fitting parameters, although, they are of course physically based. The value of the partitioning coefficient for each element is chosen after sorting the data (see § 4.3) and this is constant throughout the calculations. However, in a multi-component alloy the partitioning coefficient should change with temperature and/or composition [91] and therefore should vary along the height of the dendrites from the dendrite tips at the top of the mushy zone to dendrite roots at the bottom. Similarly the value of $\alpha$ should also vary with a temperature dependency which is however taken into account in the model (Eq. 17). However it can be seen from Figures 4.17 through 4.20 that the values of the partitioning coefficient determined from sorting the data contribute towards good fits. This can be seen in the limit of $f_s \to 0$; the experimental data and the model predictions agree reasonably well at various depths. It was therefore considered appropriate to perform a sensitivity analysis on the model’s prediction to variation in the Fourier number $\alpha$. Figure 4.27 shows the comparison between the experimental data and the predictions of the model for different values of $\alpha$ for Al, Re, W & Ta. The calculations were performed for conditions at the bottom of the mushy zone, i.e. at a depth of about 6000 $\mu$m. The values of the partitioning coefficients
used are indicated. From these plots estimates for the diffusivity $\bar{D}$ of the different elements were made using Eq. 17 and are given in Table 4.5. These are average values of the diffusivity in the corresponding range of values of $\alpha$ that yield reasonable fits to the data. The estimates for the diffusivities obtained are consistent with the findings of the authors in Ref. [120]. It can be seen from Figure 4.27 that the model is quite sensitive to $\alpha$ at higher solid fractions and diverges appreciably. This must be acknowledged as a qualification of the model. Suggestions for a possible remedy are given in the next chapter under recommendations for future work. In Figure 4.28 the numbers for the diffusivity for the three elements Re, W and Ta obtained in this way (see Table 4.5) are plotted as a function of the atomic number. Also shown are the findings of the researchers in Ref. [120]. It can be seen that the estimates for the diffusivity of Re, W & Ta obtained in this study show the same trend at a temperature of 1360°C, the solidus temperature of RR-2100, as at lower temperatures. However it must be acknowledged that the data from Ref. [120] correspond to diffusivities of the elements in pure nickel. The data obtained in this study correspond to diffusivities in the alloy RR-2100; in this light it is interesting to note that the trends for the respective diffusivities of Re, W & Ta appear to be preserved i.e. $\bar{D}_{\text{Re}} < \bar{D}_{\text{W}} < \bar{D}_{\text{Ta}}$.

<table>
<thead>
<tr>
<th>Element</th>
<th>$\alpha$</th>
<th>$\bar{D}$ [m$^2$/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>$2-3\times10^{-4}$</td>
<td>$3.7\times10^{-14}$</td>
</tr>
<tr>
<td>W</td>
<td>$8-9\times10^{-4}$</td>
<td>$1.7\times10^{-13}$</td>
</tr>
<tr>
<td>Ta</td>
<td>$6-7\times10^{-3}$</td>
<td>$1.2\times10^{-12}$</td>
</tr>
</tbody>
</table>

Table 4.5 Table showing the range of variation in $\alpha$, the Fourier number for Re, W and Ta that yield values of the diffusivity $\bar{D}$ resulting in reasonable fits to the experimental data from EPMA. $t_f = 77s$, $\lambda = 120\mu m$. 

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It was noted in Ref. [120] that the dashed lines in the data indicate that data for diffusion for the element Os was unobtainable owing to its toxicity. Their data is reproduced here with permission.

The present chapter has presented the results from the experiments that were carried out (DSC, DSQ, and EPMA) and a suitable model has been developed to interpret the data and an explanation of the physical conditions during solidification has been offered. The following chapter presents in summary the conclusions that can be drawn from the work described in this thesis and recommendations are made for future work.
Figure 4.1. Microstructure of the mushy zone of a directionally solidified specimen of RR-2100. (a) The top of the mushy zone, (b) the middle of the mushy zone and (c) towards the bottom of the mushy zone.
Figure 4.2 The measured primary dendrite arm spacings in directionally solidified specimens of RR-2100 at different cooling rates, (a) $G = 10 \, ^\circ \text{C/mm}$ and (b) $G = 6 \, ^\circ \text{C/mm}$. The theoretical prediction are after Ref. [41].
Figure 4.3. Laue Back Reflection pattern of directionally solidified RR-2100 sample. Point O is the reflection of the \{001\} plane and thus the dendrite growth direction was estimated to be about 10° away from the east-west axis.

Figure 4.4. Example of unsorted raw data obtained from the EPMA analysis of RR-2100 showing rhenium concentration in wt % vs. data point number.
Figure 4.5. Sorted EPMA data at different depths in the mushy zone. Plot shows rhenium concentration in the half-arm space at (a) 6000 μm, (b) 4800 μm, (c) 1500 μm and (d) 300 μm, from the dendrite tips. Also shown are the predictions as per the lever rule and Scheil assumptions.
Figure 4.6. Sorted EPMA data at different depths in the mushy zone. Plot shows aluminium concentration in the half-arm space at (a) 6000 μm, (b) 4800 μm, (c) 1500 μm and (d) 300 μm, from the dendrite tips. Also shown are the predictions as per the lever rule and Scheil assumptions.
Figure 4.7. Sorted EPMA data at different depths in the mushy zone. Plot shows tungsten concentration in the half-arm space at (a) 6000 μm, (b) 4800 μm, (c) 1500 μm and (d) 300 μm, from the dendrite tips. Also shown are the predictions as per the lever rule and Scheil assumptions.
Figure 4.8. Sorted EPMA data at different depths in the mushy zone. Plot shows tantalum concentration in the half-arm space at (a) 6000 μm, (b) 4800 μm, (c) 1500 μm and (d) 300 μm, from the dendrite tips. Also shown are the predictions as per the lever rule and Scheil assumptions.
Figure 4.9 Schematic illustration of changing solute concentration in a volume element under Scheil conditions, $k > 1$. 
Figure 4.10. Plot of the variation in the amounts of the gamma and the gamma prime phases in the solidifying alloy system of RR-2100 as a function of the solid fraction.
Figure 4.11. A schematic illustration of the arm space between two adjacent dendrites and its relationship with the sorting the method. The sorting method provides the concentration profile in any of the three types of volume elements shown. The sorted data could belong to Type 1, 2 or 3.
Figure 4.12. Plots of EPMA point scans showing the composition of the interdendritic regions and dendrite centres with depth into the mushy zone, for (a) rhenium, (b) aluminium, (c) tungsten and (d) tantalum in RR-2100 under conditions of a local solidification time of 77s.
Figure 4.13. Plots of EPMA point scans showing the composition of the interdendritic regions and dendrite centres with depth into the mushy zone, for (a) rhenium, (b) aluminium, (c) tungsten and (d) tantalum in RR-2100 under conditions of a local solidification time of 231s.
Figure 4.14. Plots of EPMA point scans showing the composition of the interdendritic regions and dendrite centres with depth into the mushy zone, for (a) rhenium, (b) aluminium, (c) tungsten and (d) tantalum in RR-2100 under conditions of a local solidification time of 462s.
Figure 4.15. Plots showing comparison of the weighted average obtained from the EPMA scans along horizontal lines with the data from point scans in the interdendritic regions. The figure shows the agreement between the data for composition of (a) rhenium, (b) aluminium, (c) tungsten and (d) tantalum in RR·2100 under conditions of a local solidification time of 77s.
Figure 4.16 Flowchart showing calculation procedures of the model.

Initialize variables $C_0$, $k$, $T_f$, $T_i$, $D_0$, $Q$, $\lambda$, $V$, $G$

Calculate Fourier Number $\alpha$ according to Eq. 17 for the solidification conditions

Calculate $\beta$ according to the Clyne-Kurz approximation

Compute end liquid composition according to Eq. 26

Initialize variables $\eta_s$, $\eta_s^{old}$ and Back to zero

Initialize solid concentration at all nodes to $kC_0$

Find solution to Eq. 27 using a time marching scheme, calculate value of back diffusion term using tri-diagonal matrix algorithm

$C_I \neq C_{\text{quench}}$

Update variables

$C_I = C_{\text{quench}}$

End
Figure 4.17 Model predictions for the concentration profiles of rhenium in the half-arm space at different depths in the mushy zone of RR-2100. Plots show agreement of the model predictions with the observed values obtained from EPMA at (a) 6000 μm, (b) 4800 μm, (c) 1500 μm and (d) 300 μm. The region beyond the solid – liquid interface consists of the secondary arms and the interdendritic liquid.
Figure 4.18 Model predictions for the concentration profiles of aluminium in the half-arm space at different depths in the mushy zone of RR-2100. Plots show agreement of the model predictions with the observed values obtained from EPMA at (a) 6000 μm, (b) 4800 μm, (c) 1500 μm and (d) 300 μm. The region beyond the solid – liquid interface consists of the secondary arms and the interdendritic liquid.
Figure 4.19 Model predictions for the concentration profiles of tungsten in the half-arm space at different depths in the mushy zone of RR-2100. Plots show agreement of the model predictions with the observed values obtained from EPMA at (a) 6000 μm, (b) 4800 μm, (c) 1500 μm and (d) 300 μm. The region beyond the solid – liquid interface consists of the secondary arms and the interdendritic liquid.
Figure 4.20 Model predictions for the concentration profiles of tantalum in the half-arm space at different depths in the mushy zone of RR-2100. Plots show agreement of the model predictions with the observed values obtained from EPMA at (a) 6000 µm, (b) 4800 µm, (c) 1500 µm and (d) 300 µm. The region beyond the solid – liquid interface consists of the secondary arms and the interdendritic liquid.
(a) Rhenium concentration contours in the mushy zone. EPMA data. Values in wt %.

(b) Rhenium concentration contours in the mushy zone. Model prediction. Values in wt %.
(c) Aluminium concentration contours in the mushy zone. EPMA data. Values in wt %.

(d) Aluminium concentration contours in the mushy zone. Model prediction. Values in wt %.
(e) Tungsten concentration contours in the mushy zone. EPMA data. Values in wt %.

(f) Tungsten concentration contours in the mushy zone. Model prediction. Values in wt %.
(g) Tantalum concentration contours in the mushy zone. EPMA data. Values in wt %.

(h) Tantalum concentration contours in the mushy zone. EPMA data. Values in wt %.

Figure 4.21 Concentration contours in the mushy zone of RR-2100 comparison of experimental results with the model.
Figure 4.22. Plots showing the variation in the average solid composition in the half-arm space as a function of depth in the mushy zone, for (a) rhenium, (b) aluminium, (c) tungsten and (d) tantalum. The Scheil and lever rule limiting cases are also shown.
Figure 4.23. Plots showing the variation in the liquid composition in the half-arm space as a function of depth in the mushy zone, for (a) rhenium, (b) aluminium, (c) tungsten and (d) tantalum. The Scheil and model predictions are indicated.
Figure 4.24. Optical micrograph of transverse section of RR-2100 alloy specimen. Section showing dendritic structure at a depth of 6000 μm in the mushy zone. Image shows lack of any observable eutectic nodules.
Figure 4.25 Plot showing the variation in the final concentration profile of (a) rhenium (b) aluminium (c) tungsten and (d) tantalum in a volume element at the bottom of the mushy zone in RR-2100 for different values of the Fourier number $\alpha$ as predicted by the model.
Figure 4.26 Plot showing the variation in the final concentration profile of (a) rhenium (b) aluminium (c) tungsten and (d) tantalum in a volume element at the bottom of the mushy zone in RR-2100 for different values of the partition coefficient $k$ as predicted by the model.
Figure 4.27 Plots showing the comparison between the experimental data and the predictions of the model for different values of $\alpha$ for (a) rhenium (b) tungsten and (c) tantalum at the bottom of the mushy zone in RR-2100. The plots show the sensitivity of the model to variation in the parameter $\alpha$. 
Figure 4.28 Plot showing the diffusivity of Re, W and Ta as a function of the atomic number. The data points represented by circular markers are estimates obtained in this study while the square markers represent data from Ref. [120]. The figure illustrates the similarity in the trends for the diffusivities of the elements rhenium, tungsten and tantalum between this study and an earlier study [120].
Chapter 5

Conclusions
5.1 Summary

In the literature review part of this thesis, the phenomenon of microsegregation was described in detail and the need for studying solidification in single crystal superalloys was emphasized. The mathematical models developed by various researchers for addressing back diffusion during solidification were discussed in detail, delineating the applicability and the respective drawbacks of specific models. Based on this extensive literature survey it became apparent that experimental data for the phenomenon of back diffusion in Ni–base single crystal superalloys was scarce as well as suitable models that would predict the solidification behaviour of these complex systems.

The objective of the work carried out in this thesis was to obtain experimental evidence of back diffusion in the fourth generation nickel–base single crystal superalloy RR-2100 during solidification and to develop a model that would describe the phenomenon and yield agreeable predictions of the solute profiles in the mushy zone of the alloy. Cylindrical specimens of RR-2100 superalloy were characterized first with DSC experiments to obtain evidence of the solidification path; thence the specimens were directionally solidified using a DSQ apparatus. The microstructural features of the specimens were characterized and single crystal morphology was confirmed. Solute profiles in the mushy zone of these specimens were then measured using the WDS technique in an electron probe microanalyser. A model was also developed to interpret the data and it was seen that the predictions agreed with the experimental results in a reasonable way.
The following conclusions can be drawn from the work described in this thesis:

1) It was found that the DSQ experiments were successful in freezing-in the solidification conditions during directional solidification of the specimens. The DSQ apparatus was also found to be capable of producing single crystals; this was confirmed using optical microscopy as well as with Laue back reflection.

2) The solidification range of the alloy RR-2100 was estimated using DSC apparatus and was found to be 77 K, the liquidus and solidus temperatures being 1710 K and 1633 K respectively. The solidification path of the alloy was also estimated and gave the first indication of the phenomenon of back diffusion during solidification in RR-2100.

3) The statistical sorting treatment of the EPMA data which evaluates the solid fraction on the basis of the local value of the quantity \((C_{\text{Ta}} - C_{\text{Re}})\), was found to allow for the estimation of the solidification path in the primary half-arm space. This method also allows for the calculation of the partitioning coefficients. However, this method does not have provisions for distinguishing between solute distribution in primary and secondary arm spaces.

4) Evidence for back diffusion in the primary solid in the mushy zone was found in the sorted EPMA data for composition. It was found that the average composition of the solid in the primary arm-space approached a uniform value with depth in the mushy zone, confirming the homogenizing effect of back diffusion. The average solid concentrations of aluminium and tantalum decreased with depth in the mushy zone to a uniform value while those of rhenium and tungsten increased. A
suitable model for microsegregation accounting for back diffusion in the solid phase was developed and its predictions were found to be in agreement with the experimental data.

5.2 Recommendations for Future Work

The main basis of this work has been the EPMA measurement technique, and in order to obtain meaningful information from this data the sorting method based upon difference in the local value of $(C_{Ta} - C_{Re})$ was employed and yielded the solute profiles in the half-arm space during solidification. It was found therein that a sufficient number of scans were required to be made along a horizontal line perpendicular to the dendrite growth direction at any given distance from the dendrite tips so that the data would represent the entire range of solid fractions at a particular depth. It was found for the specimen examined in this study that a total of 150 points with a spacing of 20 µm on a given horizontal line were sufficient for this purpose. However, for a specimen of different size and geometry this number may or may not suffice. Additionally, it is necessary to improve upon the sorting algorithm so that it would be possible to account for solute redistribution in secondary arms within the primary arm space. The sole purpose of these scans was to obtain data for composition in the entire mushy zone and its analysis has revealed that the phenomenon of back diffusion is present during solidification. Thus, it is recommended that future work be carried out with the aim of obtaining more precise data in the half–arm space in the form of EPMA maps that would reveal clearly the distribution of solute elements in the space between two adjacent dendrites.

This thesis has also relied upon thermodynamic databases that the software Thermocalc uses to predict phase equilibria. It was found that the
thermodynamic data for tungsten was erroneous. The model developed in this study uses partitioning coefficients for the elements that are invariant with respect to changes in temperature and composition. However, it was observed in Chapter 2 that such was not the case for multi-component alloy systems. Nevertheless, the software Thermocalc has the ability to compute phase equilibria over a range of temperatures and accounts for the changing $k's$ during solidification using its databases. Therefore, it is desirable to couple the model with Thermocalc so that computations of phase equilibrium, microsegregation and eventually even computations of freckling susceptibility can be carried out simultaneously, thereby yielding a more precise descriptions of the solidification phenomena. It is expected that such a coupled computation technique would remove the requirement for using $\alpha$ and $k$ as fitting parameters as was done in this study. This would however, entail updating of the databases to incorporate the latest experimental findings with regards to thermodynamic properties of the alloying elements and their interactions with each other during solidification.

The model developed in this study analyses diffusion in one dimension in the primary half-arm space; it is suggested finally that the model be expanded to incorporate diffusion in two dimensions. Additionally, since diffusion processes are controlled by gradients which are generally steep at the interfaces therefore an irregular mesh with a refined nodal spacing near the interfaces can be used that would minimize errors in the calculation. Alternatively, a suitable finite element mesh can be formulated that mimics the geometry of the half-arm space in terms of describing non-planar solid-liquid interfaces resulting in the growth of side arms.
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