REMOVAL OF INCLUSIONS FROM CAST SUPERALLOY REVERT

By

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We accept this thesis as conforming
to the required standard

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Abstract

It is known that the recycling of superalloy scrap causes the mechanical properties and the casting performance of reverted alloys to deteriorate. This is due to contamination of the alloy by inclusions. The contaminants affect the microstructure of the casting in terms of modification of MC carbide morphology and an increase in the amount of microporosity. Removal of such contaminants from the reverted superalloys is mandatory especially for the production of critical cast parts.

The removal of TiN and HfO₂ has been investigated in this work. The computation of the precipitation conditions for TiN in IN100 and HfO₂ in Mar-M247 has been carried out using available thermochemical data, taking into account the segregation taking place during freezing. The formation reactions are:

\[ \text{TiN}_\text{(s)} = \text{Ti} + \text{N} \]

and

\[ \text{HfO}_2 \text{(s)} = \text{Hf} + 2\text{O}, \]

where Ti, N, Hf and O are dissolved in the liquid superalloy. The solubility product for TiN precipitation in IN100 is calculated as \( \log K'_{\text{TiN}} = -2.62 \) at the liquidus temperature. The saturation solubility of nitrogen is lowered due to Ti segregation during freezing. The saturation solubility of oxygen for HfO₂ precipitation in Mar-M247 is estimated as less than 1 ppm at the liquidus temperature, and that HfO₂ particles mostly form by the reaction with the oxide crucible during remelting.

The formation and the removal mechanisms of these inclusions are examined using DS and EB remelting techniques. It is concluded that the main factor for MC carbide morphology change in IN100 is the solidification conditions not the alloy's nitrogen content.
The total nitrogen content in the liquid determines the number of TiN particles that are found as nuclei in blocky carbides. In Mar-M247, it is confirmed that HfO$_2$ is formed by the reaction with Al$_2$O$_3$ crucible during multiple remelting.

It is demonstrated that EB remelting is valid for TiN and HfO$_2$ particle removal. These inclusions are removed by a separation mechanism due to the interfacial tension forces between the particles and the liquid surface and not by a buoyancy mechanism. The saturation solubility of nitrogen for TiN precipitation in IN100 is determined to be approximately 6 ppm at the liquidus temperature which represents an aim-point for refining in recycling the alloys. Finally, the practical EBCHR conditions for removal of those inclusions are also discussed.
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Nomenclature

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<tr>
<td>AE</td>
<td>Alkaline Earth metal</td>
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<tr>
<td>( a_i )</td>
<td>Raoultian activity</td>
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<td>( a_{\text{Ti(C,N)}} ), ( a_{\text{Chinese}} )</td>
<td>Lattice parameter of Ti(C,N) or Chinese script carbide</td>
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<td>( \text{Al}_2\text{O}_3 )</td>
<td>Aluminum oxide, Alumina</td>
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<td>AOD</td>
<td>Argon-Oxygen Decarburization refining</td>
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<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
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<tr>
<td>( C_0, C_1 )</td>
<td>Initial concentration and concentration in the solid of the element</td>
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<td>CET</td>
<td>Columnar Equiaxed Transition</td>
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<td>Directional Solidification</td>
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<td>( f_i )</td>
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<td>( \Delta G^o ), ( \Delta G^i )</td>
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<td>O$_T$</td>
<td>Total oxygen content</td>
</tr>
<tr>
<td>$P_L$</td>
<td>Locat pressure of liquid metal</td>
</tr>
<tr>
<td>$P_O$</td>
<td>External pressure</td>
</tr>
<tr>
<td>$P_m$</td>
<td>Metallostatic pressure</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>Pressure drop associated with liquid metal flow through a mushy zone</td>
</tr>
<tr>
<td>$\Delta P^*$</td>
<td>Microporosity index</td>
</tr>
<tr>
<td>QDS</td>
<td>Directionally solidified and quench</td>
</tr>
<tr>
<td>R</td>
<td>Solidification rate (mm/s or m/s)</td>
</tr>
<tr>
<td>RE</td>
<td>Rare Earth metal</td>
</tr>
<tr>
<td>[S]</td>
<td>Sulfur content</td>
</tr>
<tr>
<td>$Sc/P^2$</td>
<td>Shape factor of carbide; Sc, area; P, perimeter in observed section</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon oxide, Silica</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SX</td>
<td>Single Crystal</td>
</tr>
<tr>
<td>TaC</td>
<td>Tantalum carbide</td>
</tr>
<tr>
<td>𝑇_c, 𝑇_b, 𝑇_l</td>
<td>Carbide formation, 𝛾-𝛾' eutectic formation, liquidus temperature, respectively</td>
</tr>
<tr>
<td>TiC</td>
<td>Titantium carbide</td>
</tr>
<tr>
<td>Ti(C,N)</td>
<td>Titanium carbonitride</td>
</tr>
<tr>
<td>TiN</td>
<td>Titanium nitride</td>
</tr>
<tr>
<td>𝑡_p</td>
<td>Theoretical time required for a particle to float or sink (s)</td>
</tr>
<tr>
<td>𝑡_R</td>
<td>Residence time of a particle in a hearth (s)</td>
</tr>
<tr>
<td>Δ𝑇</td>
<td>Solidification range</td>
</tr>
<tr>
<td>V̇</td>
<td>Local flow velocity</td>
</tr>
<tr>
<td>VAR</td>
<td>Vacuum Arc Remelting</td>
</tr>
<tr>
<td>VIM</td>
<td>Vacuum Induction Melting</td>
</tr>
<tr>
<td>V_p</td>
<td>Terminal velocity of a particle</td>
</tr>
<tr>
<td>WDX</td>
<td>Wavelength Dispersive Spectrometer</td>
</tr>
<tr>
<td>ZrSiO₄</td>
<td>Zircon</td>
</tr>
<tr>
<td>𝛼</td>
<td>Particle removal efficiency</td>
</tr>
<tr>
<td>𝛾</td>
<td>Austenite matrix</td>
</tr>
<tr>
<td>𝛾'</td>
<td>Gamma prime, Ni₃(Al,Ti)</td>
</tr>
<tr>
<td>𝛾''</td>
<td>Gamma double prime, Ni₃(Nb,Al,Ti)</td>
</tr>
<tr>
<td>𝜌_L</td>
<td>Density of a liquid</td>
</tr>
<tr>
<td>𝜌_S</td>
<td>Density of a solid</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\Delta \rho$</td>
<td>Density difference between a particle and liquid metal (Kg/m$^3$)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity of liquid metal (cps.)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Tortuosity of dendrites</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Specific area of solid/liquid interface</td>
</tr>
</tbody>
</table>
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1. Introduction

Nickel base superalloy is one classification of the superalloys that have been developed for high temperature services, where relatively severe mechanical stresses are encountered and where surface stability is frequently required [1]. Nickel base alloys possess superior, high temperature capabilities: high strength, high low cycle and high cycle fatigue resistance, and creep resistance at elevated temperature. They are, therefore, used for applications such as gas turbine engines, whether for industrial or aero applications. Their outstanding characteristics at elevated temperature come from well-developed chemical compositions and closely controlled manufacturing processes. While the superalloys take advantage of several strengthening mechanisms to improve their strength, precipitation hardening by fine intermetallic particles, gamma prime $\gamma'$, $\text{Ni}_3(\text{Al},\text{Ti})$, or gamma double prime $\gamma''$, $\text{Ni}_3(\text{Nb},\text{Al},\text{Ti})$, contributes mainly to their high strength in a high temperature environment. In contrast to their high strength at elevated temperature, however, nickel base alloys have relatively poor fracture toughness and are consequently susceptible to failure.

It has been reported [2-6, for example] that the fatigue and mechanical properties of the nickel base alloys are limited by defects: non-metallic inclusions, segregation, porosity, etc. (Figure 1.1) These defects are introduced from raw materials or by chemical reactions during melting and casting processes. In addition to the defects, carbide itself, which is the main constituent of superalloy structure, becomes an initiation site and a path for fatigue cracks when its size and shape are not appropriate [7]. The harmful defects must be eliminated from products, especially from rotating parts used for aero-engine components, in order to guarantee fatigue properties and to make the residual life accurately predictable. From this point of view, it is important in the production of clean superalloys for critical
Chapter 1 Introduction

Inclusion diameter, $d_m$

a) Calculated dependence of inclusion diameter on fatigue life.

$K_{IC}$, MPa$m^{1/2}$

b) Calculated dependence of $K_{IC}$ on inclusion number density.

Figure 1.1 Effect of inclusions on fatigue properties of superalloy. a) Calculated dependence of fatigue life on inclusion diameter for two different superalloys: One is a relatively strong P/M superalloy and the other is a relatively weak wrought superalloy, b) Calculated dependence of $K_{IC}$ on inclusion number density [3].
Chapter 1 Introduction

applications, for which higher fatigue resistance is required, to select high-grade raw materials and appropriate melting, refining and casting processes. Vacuum melting and refining carefully monitored and related techniques are generally employed in the superalloy industry. During refining, nonmetallic inclusions and harmful impurities will be eliminated from the melt, and well-controlled structure can be obtained during casting under the suitable conditions.

The requirements for clean superalloys, however, have not been satisfied completely since the demands for increased strength, increased toughness and increased temperature capability are being continuously increased. To meet the demands, the concept of superclean or zero defect superalloy manufacturing has been proposed [8-13]. The concept is to start from the premise that all engineering materials contain defects and to reduce the number of defects as much as possible: the ultimate goal is to reduce the number of defects to zero.

In connection with soundness of nickel base superalloys, the issue which must be considered is recycling of superalloy scrap. There are a number of reasons why recycling is practiced by superalloy industry, particularly castings: the large amount of scrap that the industry itself generates, the price fluctuation and the availability of the critical raw materials used in nickel base superalloys. For instance, throughout the industry, the weight of semi-finished products of wrought alloy is less than one third of the weight of alloy melted. Some complex machined components may have a final product yield of less than 10 %, or approximately 50 % of the materials input actually end up as parts in a typical investment casting process.
Chapter 1 Introduction

The scrap contains valuable and recoverable alloying elements. The elements of concern are the strategic metals such as chromium, cobalt, nickel, tungsten, molybdenum, niobium, hafnium and tantalum, which are contained in nickel base superalloys in substantial quantities. It is clear that fluctuation of the price and shortages of such critical elements directly affect manufacturing of superalloys. From these points of view, it has become common practice in the superalloy melting industry to make maximum use of scrap as a raw material, since scrap metal is usually less expensive than primary metals and more readily available.

In contrast with the advantages of the low price and availability of the scrap, there is disadvantage of scrap use, i.e., manufacturing of reverted superalloys that are produced from recycled scrap or from mixture of the scrap with virgin metals. In a practical sense, the recycled scrap may be contaminated by oxides, nitrides, etc. The contaminants in the scrap used result in the formation of the defects: in most cases, the content of non-metallic inclusions or microporosity is increased. Consequently, in the typical recycling of superalloy, vacuum induction melting of the foundry reverts does not produce alloys of the same mechanical properties that virgin alloys do because of an increase in these defects. Used parts are not normally recycled because of the contamination from coating, brazing and welding and direct recycling of superalloys for some applications such as those for rotating parts in gas turbine engines is effectively excluded. Reverted superalloys have not yet been approved for critical cast parts or components due to their unsatisfactory soundness.

In this thesis, the objectives of this work and selection of materials are given in Chapter 2, the pertinent literature is discussed in Chapter 3, a description of the experimental equipment and methods is given in Chapter 4. Experimental results and discussion are shown in Chapter 5. Finally, the conclusions are presented in Chapter 6.
Chapter 2  Objectives

2. Objectives

2.1. Objectives of This Work

The objectives of this work are to investigate the mechanisms and the effects of the removal of non-metallic inclusions from reverted cast superalloys. The principal questions to be answered are:

1) What is the role of nitrogen in producing microporosity in reverted alloys?
2) What is the main removal mechanism for oxide inclusions during melting of reverted alloys?

We have chosen two example alloys: IN100 and Mar-M247 in which we find principally titanium nitride (TiN) and hafnium oxide (HfO₂), in the reverted superalloys, to determine the mechanisms of avoiding the metallurgical problems caused by them, and to estimate the conditions necessary for the removal of inclusions from the cast superalloy revert, using electron beam remelting method.

2.2. Selection of Material

For this work, two specific alloy systems are selected for investigation of inclusions of the interest: IN100 for TiN removal and Mar-M247 for HfO₂ removal. The nominal compositions of both alloys are listed in Appendix A.

The alloys, IN100 and Mar-M247, are well known as alloys for cast turbine blades. IN100 is principally used as a DS alloy; Mar-M247 as both DS and SX castings. Since IN100 is one of few alloys which contains vanadium, its scrap is only recycled to itself or downgraded to high-alloy steel. It is also known to be susceptible to casting porosity, and
it is suggested that high nitrogen content promotes this susceptibility. It is therefore
difficult to revert due to its tendency to porosity and is mainly used in reverted form as mixed
virgin/revert combination. Mar-M247 is a hafnium-bearing alloy and is used mainly in aero
turbines. This alloy is less sensitive to porosity and is known to give reasonable
performance in the reverted condition. However, due to the strong affinity of hafnium to
oxygen, hafnium oxide will form when sufficient oxygen is supplied, e.g., from melting or
casting refractories, and will act as harmful inclusions. Hafnium oxide is of particular
interest because it is more dense than the liquid superalloy and therefore develops a negative
buoyancy force.

The formation of TiN depends on thermochemical and compositional relationships,
and TiN has been discussed particularly in relation to microporosity and carbide morphology
in superalloy castings. Since the nitrogen contents of reverted alloys are normally higher
than of virgin, it is expected that TiN will form easily in reverted alloys.

In reverted alloys, greater amounts of microporosity and blocky type carbides are
commonly observed, and it is suggested that they result from the existence of TiN, relating to
high nitrogen content. With regard to microporosity, it is implied that relatively large
blocky carbides with TiN cores prevent the residual liquid from feeding into the interdendritic
region.

For the removal of TiN in order to avoid such problems in reverted castings, not only
the separation of existing TiN (e.g., flotation) but also the thermochemical conditions, at
which TiN precipitation is avoided or TiN becomes soluble, must be taken into consideration,
in relation to solidification condition.
In this thesis, the formation of TiN associated with solidification, carbide morphology and microporosity will be discussed. The critical levels of nitrogen, at which TiN formation can be eliminated, are also estimated.

Hafnium has strong affinity to oxygen as well as the other reactive elements such as aluminum, titanium and chromium contained in superalloys do. HfO$_2$ is considered to form during melting or remelting due to the reaction of hafnium with oxide refractories rather than the precipitation during solidification because oxygen content in superalloy is normally very low. Such HfO$_2$ will be retained in reverted alloys and affect the properties.

It is commonly suggested in the electron beam remelting process that separation by the density difference between particle and the melt is the important factor. However, interfacial tension force, in practice, affects the particle separation significantly, and it is assumed to be strong enough to keep the particles on a free surface even if the relative buoyancy is negative.

In this project, the formation of HfO$_2$ in the superalloy will be estimated in regard to thermochemistry, and also the dominant mechanism for the separation from the liquid alloy will be investigated.
3. Literature Review

3.1. Melting Practice of Superalloy

Nickel base superalloys are divided into two categories in terms of their processes: cast superalloys and wrought superalloys. In aerospace applications, cast superalloys are mostly applied for turbine blades due to the combination of high temperature capability and strength. Wrought alloys are used for parts such as wheels, disks, cans and liners.

Melting of both superalloys for aerospace use generally takes place in two or three steps, and the melting practice utilized is a combination of the following vacuum melting and remelting processes such as Vacuum Induction Melting (VIM), Electron Beam (EB) Remelting, Vacuum Arc Remelting (VAR) and Electro Slag Remelting (ESR). Lherbier [14] has described the melting and refining of superalloys in detail. Figure 3.1 shows operating pressure range of these processes relative to other vacuum techniques [15]. After melting or remelting processes, the cast superalloy is normally supplied for investment casting process operation under vacuum in most cases of airfoils. In the case of wrought alloys, the ingot produced by a combination of melting and remelting operations is offered for forging or rolling processes. While the interests of this project are in cast superalloy, the typical processes for both cast and wrought superalloys will be described.

3.1.1 Cast Superalloy

Cast superalloy is primarily melted from raw materials using vacuum induction melting (VIM). Electron beam (EB) remelting is sometimes employed after the VIM operation. The alloy, whose chemical composition is closely controlled, is made by the vacuum casting process and undesirable impurities are removed.
**Figure 3.1** Operating pressure range of vacuum process [15]
3.1.1.1. Vacuum Induction Melting (VIM)

VIM process has been the primary melting method for both cast and wrought superalloys because of its ability in close chemical control and homogeneity of the melt. The complete melting and mixing of charge materials due to a relatively long melting time is essential to obtain the required constant compositions. A typical VIM cycle starts with the charging of either virgin raw material or scrap. Following the pumping down, the charged materials are melted. When the metal becomes completely molten and the bath is stable, desulfurizing or deoxidizing additions are made. Then, reactive elements are added, and finally, the melt is cast when its composition is appropriate.

The impurities, which have high vapor pressure such as Pb, Bi, Te, Se and Cu, are removed to the level at which they become harmless to the properties of the alloys by evaporation reaction and gas phase reaction during melting [15]. Deoxidation is achieved by carbon boiling and addition of aluminum and alkaline earth (AE) or rare earth (RE) metals, as shown in Figure 3.2 [16]. Addition of calcium, magnesium or rare earth metals accomplishes desulfurization of the melt (Figure 3.3 [16]).

In spite of its ability to adjust composition and refine impurities, VIM is the only vacuum melting method which uses a refractory crucible made of oxides such as MgO, Al$_2$O$_3$, and MgO-Al$_2$O$_3$ spinel. Unfortunately, the use of refractory causes a problem; that of metal/refractory reaction leading to crucible disintegration producing exogenous oxide inclusion agglomerations in the melt. Since pouring of the melt is carried out by tilting the furnace, in most cases oxide inclusions in the melt or floating on the melt surface are carried into the mold and entrapped in the bulk solid. This drawback has led to the introduction of special tundish designs with ceramic filters.
Figure 3.2 Variation of oxygen activity $a_o$ and total oxygen content $O_t$ during vacuum induction melting of alloy 718 using virgin and revert charges; md, melt-down; r, end of refining period; other symbols on horizontal axis represent element additions to melt [16].
Figure 3.3 Reduction in sulfur content [S] during vacuum induction melting [16].
The advantages of the filtering technique on inclusion removal are reported in the literature [for example, 17, 18].

It is, however, still difficult to control the ceramic filtering operation. The solubility of inclusions, e.g., Al₂O₃, and TiN, is usually temperature dependent. When the pouring (melt) temperature is high enough for inclusions to dissolve into the melt, the ceramic filter cannot collect them and they will re-precipitate in the alloy during solidification. On the contrary, when the pouring temperature becomes low enough to avoid dissolution of inclusions, filter clogging may occur. In the worst case, breakage of the filter will occur. The control of the pouring (melt) temperature in a narrow range is critical and a difficulty in filtering practice.

Since VIM process is principally melting process, it can not control the solidification of the melt. The cast ingot has relatively large pipes, pores and segregation after the melt is cast into the mould under vacuum. Such pipes and pores sometimes cause inclusion problems when the cast is used for melt stock in investment casting due to the entrapment of abrasive or other unwanted particles in these crevices. Remelting process can eliminate these defects.

3.1.1.2. Electron Beam (EB) Remelting

Electron Beam (EB) remelting has recently emerged as an alternative for superalloy refining due to its remarkable ability to remove the impurities and inclusions. The process, usually applied in the form of a Cold Hearth Refining (EBCHR) furnace, offers more flexibility as to melting rate and ingot shape than the VAR process, since the heat source is independent of the charge material. In EBCHR process, melting, refining and casting
Chapter 3  Literature Review

(solidification) are operated separately in vacuum chamber. In each stage, temperature is well controlled by the electron beam as a heat source.

Many researches [19-27] have been carried out in order to evaluate the EB process capabilities for the production of clean products to be used for aerospace components. In general, the results from these studies have been very promising and show much improved cleanliness levels compared to the other processes such as VIM, VAR and ESR. In these studies, the EB button melt technique is applied for the evaluation of cleanliness of the material, and has been standardized in ASTM. The detail of EB button technique is described in Appendix B. Table 3.1 shows oxide inclusion content results of two types of superalloys for various ingot melt practices. It is obvious from Table 3.1 that VIM/EBCHR can produce the cleanest ingot.

The remarkable refining capability of the EBCHR process is also an advantage in the case of scrap remelting. Figure 3.4 [28] illustrates the cleanliness improvement of Rene 125, which contains 1.5 wt.% hafnium, by the EBCHR process compared with the VIM process in terms of normalized oxide raft area (NORA), which is the area on the EB button surface covered by oxides per unit weight. The result shows the EBCHR process is effective not only in remelting of recycled materials but also in virgin alloy.

After the melting step in the EBCHR process, refining of the melt can be carried out in the water-cooled copper hearth under a high vacuum environment. Removal of impurities or inclusions is carried out by volatilization and separation by the density difference of the melt and the inclusions and also by surface or interfacial tension forces.
Table 3.1 Oxide inclusion content results for various ingot melt practices by EB button melt test SEM/EDS/IA(1) technique [19,24]

<table>
<thead>
<tr>
<th>Process</th>
<th>Particle/lb. Button wt. (&gt;25.4μm)</th>
<th>Largest oxide particle size (μm)</th>
<th>Major oxide element</th>
<th>Total oxide content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN718</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- VIM</td>
<td>485±92(2)</td>
<td>668±150</td>
<td>Al, Si, Ti, Ca</td>
<td>2.9±0.1</td>
</tr>
<tr>
<td>- VIM/VAR</td>
<td>143±142</td>
<td>281±218</td>
<td>Al, Ca, Ti</td>
<td>1.4±0.9</td>
</tr>
<tr>
<td>- VIM/ESR</td>
<td>20±13</td>
<td>68±12</td>
<td>Al, Si, Ca</td>
<td>0.6±0.4</td>
</tr>
<tr>
<td>- VIM/EBCHR</td>
<td>1±1</td>
<td>37±28</td>
<td>Al, Si, Ca</td>
<td>0.1±0.1</td>
</tr>
<tr>
<td>Rene 95</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- VIM</td>
<td>125±122</td>
<td>257±69</td>
<td>Al, Ti, Ca, Si</td>
<td>1.3±0.9</td>
</tr>
<tr>
<td>- VIM/VAR</td>
<td>267±157</td>
<td>163±64</td>
<td>Al, Ti, Ca</td>
<td>2.8±2.3</td>
</tr>
<tr>
<td>- VIM/ESR</td>
<td>42±29</td>
<td>94±52</td>
<td>Al, Ti, Ca</td>
<td>0.6±0.2</td>
</tr>
<tr>
<td>- VIM/EBCHR</td>
<td>10±5</td>
<td>109±48</td>
<td>Al, Ti, Ca</td>
<td>0.2±0.3</td>
</tr>
</tbody>
</table>


(2) All ± variations shown are for one standard deviation.
Figure 3.4 The cleanliness improvement of Rene 125 by EBCHR process [28].
In the case of separation by the density difference between the melt and the inclusions, low density inclusions float up to the melt surface and are retained by surface tension force. High density inclusions sink and are retained in the skull. The terminal velocity, $V_p$, of particles in the molten alloy can be determined by Stoke's Law [29]:

$$V_p = \frac{\Delta \rho g d^2}{18 \mu}$$

(3.1)

where $\Delta \rho$ is the density difference between the particle and the liquid metal (Kg/m$^3$), $g$ is gravitational constant (m/s$^2$), $d$ is a particle diameter (m) and $\mu$ is a liquid metal viscosity (cp.). Assuming that the pool depth of the hearth is $H$, the theoretical time, $t_p$, required for a particle to float or sink is:

$$t_p = \frac{H}{V_p}$$

(3.2)

If $t_p$ is small compared to the residence time of the liquid metal in the hearth $t_R$, the particle removal efficiency $\alpha$ is expected as:

$$\alpha = 1 - \exp\left(\frac{t_R}{t_p}\right)$$

(3.3)

The other important mechanism in inclusion separation is interfacial tension force between the liquid metal and the particle (see Appendix C). The interfacial tension force is expected to be large enough to retain the inclusions on the liquid surface. Such inclusions are collected and separated from the melt by the mechanical or electrothermal barrier.

The interfacial tension force of the liquid metal is estimated to be about 500 dyn/cm (0.005 N/cm) [30] which is large enough for almost all types of inclusions to be retained on the surface. It is therefore readily seen that an inclusion, whose density is greater than that of the melt, can be captured on the liquid surface and can be removed from the alloy melt.
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For example, it is reported [25,28,31] that hafnium oxide (HfO₂) particles that have a density of about 10 g/cm³ are found at the raft area of EB melted button surface. The major mechanism of separation by interfacial tension force will be explained as:

1) When the surface of the melt stock is melted by the electron beam, the inclusion particles are captured at the surface of molten layer by interfacial tension forces.
2) After the molten metal falls to the liquid pool in the cold hearth, the tension forces keep inclusion particles retained on the liquid pool surface.
3) The inclusions retained on the liquid surface are collected by the barrier, and separated from the alloy melt.

Despite the mechanisms of inclusion removal mentioned above, there is a difficulty in separation of certain types of inclusions. The inclusions that have dissolved in the melt can not be removed. Since the solubility of most of inclusions is temperature dependent, they may dissolved into the liquid alloy when the temperature is excessively high. The problem is that the elements solutioned will re-combine and re-precipitate with decreasing the temperature during solidification, and that they will affect the properties of the alloy. In order to prevent this, the temperature of the melt must be kept as low as possible, and if the solubility of the element is pressure dependent, e.g., nitrogen, operating pressure must also be maintained as low as possible.

The flexibility for shape of feed stock is another advantage of the EBCHR furnace. Since either bar stock or scrap metal can be fed into the melting stage, one particular interest is for the recycling of superalloy scrap. The scrap metals contaminated significantly by unwanted compounds must be refined before remelting. At refiners of superalloys [32], the scrap metals are usually processed by additional refining methods such as argon-oxygen decarburization refining (AOD) process or VIM process. With the remarkable refining capability of the EBCHR process, however, it is possible to refine the scrap metals directly.
Chemical change in contents of elements such as chromium, manganese or aluminum during processing is the major drawback of EBCHR process. In the EBCHR system, the principal chemical changes take place in the hearth volume [33,34]. The hearth metal volume experiences a much greater time × temperature function than does ingot pool at the same melting rate. This results in enhancement of evaporative chemical changes in bulk composition.

3.1.1.3. Investment Casting

There are a number of casting processes available to provide near-net-shape superalloy cast parts. All such products have been essentially produced by the investment (precision) casting process under vacuum condition. The advantages of the casting process are closely controlled dimensions, an ability to produce stronger high-temperature alloys that contain high amount of strengthening elements and are not amenable to hot forging, and fine surface finishes. The advances in this process have made possible the casting of complex shape blades, which contain air passages for cooling. At present, aircraft manufacturers specify the investment casting process for the manufacture of critical turbine blades.

The basic investment casting process is in general constituted by the following steps.

1) Make a wax or plastic pattern of the piece and add to it the gates, runners and other parts of the molten metal distribution system. Make a ceramic core to be inserted into the die cavity, if the product contains internal passages.

2) Dip the assembly in a thin slurry of mold refractory, cover with granular ceramic stucco to strengthen the shell. Repeat this step to develop a rigid shell.

3) Dry the assembly slowly.
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4) Heat the mold/pattern assembly to melt out the wax pattern, fire the mould to increase the strength.
5) Attach an insulating bracket to minimize the heat loss and to control solidification, and then preheat the mould.
6) Start the melt in the vacuum furnace and pore the molten metal into the mould.
7) Remove the mould, cut off the gates, runners, etc. after solidification has finished and the casting has cooled.

The shell materials are selected depending on a number of parameters such as alloy, temperature, casting process and cost. Some of the typical refractory materials are alumina (Al₂O₃), silica (SiO₂), zircon (ZrSiO₄) and aluminosilicate. The binder is critical to the stability and rheology of the ceramic slurry and green and high temperature strength of the shell. Either colloidal silica or ethyl silicate is used as the binder for most superalloy investment shell moulds.

Directional solidification (DS), columnar grained and single crystal, techniques are applied for turbine airfoil castings because of the higher capability at elevated temperature. Figure 3.5 shows comparison of creep properties of Mar-M200 in conventionally cast, directionally solidified and single crystal forms [35]. DS castings are essentially produced using vacuum casting equipment in which the alloy charge is melted in an isolated chamber, and the pressure is maintained at 10⁻³ ~ 10⁻⁴ torr for pouring.

Directional solidification is accomplished in vacuum, as shown in Figure 3.6, by pouring the molten alloy into a preheated, ceramic shell mold that is open at the bottom and sits on a water-cooled copper chill plate [36]. After thin layers of equiaxed grains forms on the chill plate, solidification proceeds in a directional manner in a columnar grain starter block as a consequent of the thermal gradient that created between heated (molten) melt in the
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Figure 3.5 Comparison of creep curves for Mar-M200 in conventionally cast, directionally solidified and single crystal forms [35].

Figure 3.6 Directional solidification process [36]. a) Columnar grain casting process; b) single-crystal casting process.
upper portion of the mould and the chill plate. In order to control the heat extraction, the water-cooled chill plate is lowered, withdrawing the mould from the heating furnace when solidification starts. In the case of single crystal casting, one grain is selected from columnar grains by single crystal selector, which acts as a grain filter.

It is well known that commonly occurring defects during casting are nonmetallic inclusions, shrinkage porosity, unwanted grain morphology, hot tears and cold shuts. Nonmetallic inclusions are the largest single cause of rejected castings in the industry because the control of inclusions can only be achieved by paying very careful attention to detail throughout the manufacturing process. The other defects may be avoided to a large extent by re-engineering of the shell and mold design, modification of casting parameters and the alloy design.

Inclusion control of the alloy commences with the supplier of melting stock. The major cause of inclusions is the ceramic refractory of the VIM furnace in both stock supplier and casting foundry [37]. To avoid this, the alloy melted in the VIM furnace goes through a ceramic filter during pouring. However, the operation of filtering is still critical and not stable. In case of the VIM furnace in investment casting, bottom pouring instead of tilting can prevent the entrainment of the impurities floating on the top of the molten pool into the cast component. Figure 3.7 shows a schematic diagram of a vacuum investment casting furnace featuring the bottom pouring method [37]. Bottom pouring practice is mostly used for small melt weights and is applied in high-productivity single-purpose facilities.

Another cause of inclusion problems is the reaction with refractory shell or mould during casting and solidification. The molten alloy usually contacts with the pre-heated shell mould made by ceramics for a period enough to cause a reaction between the reactive constituents and oxides.
**Figure 3.7** Schematic diagram of an investment casting unit with bottom pouring furnace. 1, ceramic crucible; 2, induction coil; 3, resistance heater; 4, baffle; 5, power feedthrough; 6, chill plate; 7, withdrawal chamber [37].
The inclusions formed, oxides in most case, are retained in the castings and result in the deterioration of high-temperature capabilities of the alloy.

3.1.2 Wrought Superalloy

In the case of wrought superalloys, melting and remelting processes also play a role in the ingot production. Since VIM, which is the primary melting process, can not control a solidification structure, the VIM ingot contains significant segregation and pipes. It is therefore usually remelted by VAR and/or ESR processes to improve cast structure and cleanliness, and then supplied for hot working processes such as forging and rolling.

3.1.2.1. Vacuum Arc Remelting (VAR)

Aerospace grade superalloys are frequently produced via VIM and Vacuum Arc Remelting (VAR). VAR is basically consumable electrode melting under vacuum. In VIM-VAR processing, VIM supplies cast electrode. In VAR process, chemical interference and introduction of oxide inclusions from refractories can be avoided since the melting and solidification take place in a water-cooled copper crucible. The VIM-VAR sequence combines the chemical control of the VIM process and the solidification control with low macro and microsegregation of the VAR process.

The VAR technique is a well-established one, and melting conditions are closely controlled and monitored. However, improper melting parameters sometimes cause macrosegregation defects. Major defects found in VAR processed alloys are freckles and white spots. Both types of defects can initiate premature failure.
Freckles, the solute-rich segregation defects, are sometimes found especially in the niobium-bearing alloys, e.g., IN718. They are niobium rich regions with excessive amount of Laves phases, Fe$_2$(Nb,Ti). Freckles result from processing at a relatively high melt rate and from the flow of solute-rich interdendritic liquid in the mushy zone during solidification [38]. The ways to avoid freckles are to control the melt rate so maintaining the mushy zone and local solidification time short enough to prevent their formation and to improve the ingot heat extraction rate resulting in a decrease of the local solidification time.

White spots are also macrosegregation defects in which the solute is more depleted in alloy elements such as Nb and Ti than the matrix. Mitchell [39,40] concluded that the formation of white spots is due to following three reasons:

1) A relic of unmelted electrode dendrites, originally introduced during VIM processing.

2) A piece of crown region, formed by condensed vapor and spattering droplets, which had fallen into the melt and not dissolved or melted.

3) A piece of the shelf region, formed at the pool surface periphery, which was undercut by the unstable arc movement and swept into the solidifying interface.

White spots are usually found at the billet stage of processing and are normally associated with inclusion clustering, cracking and porosity. In order to minimize their occurrence, the factors which must be controlled are maximum melt rate permitted by ingot microstructure, a short arc gap to minimize crown formation and to maximize arc mobility and attention to electrode structure.

3.1.2.2. Electro Slag Remelting (ESR)

Electro Slag Remelting (ESR) is consumable electrode melting using water-cooled copper crucible. While the electrode is melted under the atmosphere, the molten pool is
isolated from the atmosphere by a covering of slag between the electrode surface and the molten pool surface. Although this process was originally devised as a solidification control process for superalloys, it was expanded in general applications due to its significant ability to improve the cleanliness of the alloy. It is generally stated that alloys melted by ESR process exhibit no memory for the inclusion content of the electrode and that the tolerance for poor electrode is a very strong advantage of this process.

The inclusion content in a processed ingot is established entirely by alloy composition, slag composition and ESR deoxidization practice. Sulfide and oxide inclusion contents are greatly reduced by ESR. However, the problem of nitride removal still remains since nitride, e.g., TiN, is not soluble in the slag. TiN is rejected to the electrode/slag interface upon melting and consequently to the rim of the ingot surface by the force operating on the ingot pool meniscus. Addition to above, since the remelting is carried out under air, nitrogen pick-up occurs in case of a low nitrogen electrode through the slag. It is reported that nitrogen content of the ingot is reached to about 60 ppm in case of IN718 whether that of the electrode is lower or higher than the level of 60 ppm [40].

The high tolerance of ESR for electrode is accepted into triple melt process, VIM-ESR-VAR process. In triple melt process, ESR process uses the electrode melted by VIM with well-adjusted composition and contributes to the reduction of sulfur content, the removal of inclusion agglomerations and entrapped slag and the production of a fully-densed structure without pipes or cavities. This ingot is then used as the VAR electrode to control final ingot structure.

As a summary of melting practice, Table 3.2 [24,41] lists the advantages and disadvantages of melting and remelting processes of superalloys.
Table 3.2 Summary of melting or remelting process [24,41].

<table>
<thead>
<tr>
<th>process</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIM</td>
<td>• Refine material</td>
<td>• Introduces ceramics</td>
</tr>
<tr>
<td></td>
<td>• Good chemistry control</td>
<td>• Poor structure control</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Pipe and segregation</td>
</tr>
<tr>
<td>VAR</td>
<td>• Structure control</td>
<td>• Segregation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Freckles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• White spots</td>
</tr>
<tr>
<td>ESR</td>
<td>• Structure control</td>
<td>• Potential for slag entrapment</td>
</tr>
<tr>
<td></td>
<td>• Improved cleanliness</td>
<td>• Potential for center segregation</td>
</tr>
<tr>
<td></td>
<td>• Potential for white spots reduction</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Reduction on S content</td>
<td></td>
</tr>
<tr>
<td>EBCHR</td>
<td>• Cleanest process</td>
<td>• Currently asymmetric structure</td>
</tr>
<tr>
<td></td>
<td>• Potential for best structure control</td>
<td>• Segregated skin</td>
</tr>
<tr>
<td></td>
<td>• Amenable to good process control</td>
<td>• Evaporation losses</td>
</tr>
<tr>
<td></td>
<td>• Flexibility for feed materials</td>
<td></td>
</tr>
</tbody>
</table>
3.2. Superalloy Scrap and Recycling

Approximately 55 million pounds of clean and contaminated superalloy scrap were processed in 1986 [32]: about 70% was recycled into the same superalloy, 20% was downgraded, and 10% was sold to refiners. The average contents of the elements in superalloy scrap was about 44% Ni, 16% Cr, 5% Co, 2% Nb, less than 1% each of Mn and Ta. The remaining 30% was primarily Al, Fe, Mo, Ti, W, and other minor constituents.

The superalloy scrap is usually classified into three types: home scrap, prompt industrial scrap and obsolete scrap [42,43], as listed in Table 3.3. While home scrap is relatively clean, obsolete scrap contains the significant amount of contaminants such as oxides, nitrides and corrosion products that are formed during service.

Figure 3.8 [32] shows the material flow circuits of cast and wrought superalloys, respectively. The difference in material flow between cast and wrought alloys is the amount of scrap recycled into the circuit: 50% of raw material is primary metals in cast alloy; in wrought alloys, 33% is composed of primary metals. The use of scrap for cast alloys is presently decreasing because of two major reasons. One reason is improved product yield due to casting nearer to finished dimensions, and the other is considered to result from the imposition of more stringent chemical specifications for rotating parts by engine manufactures that exclude previously used scrap.
Table 3.3 Types of superalloy scrap [42,43].

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Home scrap</td>
<td>Scrap generated by an alloy producer during the primary product manufacturing process.</td>
</tr>
<tr>
<td>Prompt industrial scrap</td>
<td>Scrap generated by fabricators or manufacturers during conversion of a primary product to a finished product at a location removed from melting facility.</td>
</tr>
<tr>
<td>Obsolete scrap</td>
<td>Scrap generated when used equipment is overhauled or dismantled.</td>
</tr>
</tbody>
</table>
a) Cast superalloys

Figure 3.8 Material flow circuit of cast and wrought superalloys in 1986 [32].
b) Wrought superalloy

Figure 3.8 Material flow circuit of cast and wrought superalloys in 1986 [32]. (continued)
3.3. Properties of Reverted Superalloy

Recycling of superalloy scrap plays an important role in its cost and availability as a raw material, however, reverted cast superalloys have been prohibited for use in critical applications such as rotating parts in aircraft engines. That is because the mechanical properties of reverted alloys are usually inferior to those of virgin alloys due to the residual contaminants from scrap that become origin of the detrimental defects. These contaminants modify the alloy composition, and affect solidification behavior, microstructure, foundry performance and mechanical properties consequently.

3.3.1. Chemical Composition

It is suggested [44-48] that, compared with virgin alloy, the element most significantly different in reverted alloy is nitrogen and that the nitrogen level in VIM processed reverted alloy is at least twice the level in virgin alloy in typical cases, as shown Table 3.4. It is assumed that the source of nitrogen in reverted alloy is the scrap used for remelting. The widely held assumption is that the vacuum casting reacts with the gases evolved from the mold during pouring which results in castings with higher nitrogen content particularly at the surface [44,47]. Figure 3.9 shows the nitrogen levels of IN100 scrap.. The large surface areas of blade airfoil contain a very high level of nitrogen compared with the root section: 90 ppm nitrogen at the blade surface and 5 ppm at root section.

Lamberights et al. [45] reported that scrap recycling in the case of IN100 does not affect oxygen level in a consistent way, as shown in Figure 3.10. The reason for the equivalent oxygen level between virgin and revert is assumed that deoxidation reaction will effectively carried out during remelting in VIM furnace.
Table 3.4 Comparison of nitrogen levels in virgin and revert turbine blades [44].

<table>
<thead>
<tr>
<th>Material</th>
<th>Revert</th>
<th>Virgin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>R</td>
<td>A</td>
</tr>
<tr>
<td>R=root</td>
<td>1 2</td>
<td>1 2</td>
</tr>
<tr>
<td>A=airfoil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blade No.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15 12</td>
<td>17 24</td>
</tr>
<tr>
<td>N₂ (ppm)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Uncertainty of nitrogen analysis is expected to be ±3 ppm.

Airfoil Surfaces 90 ppm  
Root Section 5 ppm  
Runner/Feeder Bar Surface 11 ppm  
Header from Pouring Basin 2 ppm

Figure 3.9 Nitrogen levels of IN100 scrap [44].
Figure 3.10 Master-melt quality and gas content. V1, virgin; V1i, chromium nitride inoculated virgin; R1, revert; R2*, foundry scrap revert; R**, chemi-machined scrap revert. V1i, R2* and R** were remelted in the laboratory VIM furnace [45].
3.3.2. Microstructure

The microstructure of cast superalloys generally consists of coherent $\gamma'\text{-Ni}_3(\text{Al,Ti})$ precipitates in a $\gamma$ dendritic matrix with MC type carbide particles distributed along or between dendrite arms as well as grain boundaries and the $\gamma'$-$\gamma$ eutectic generally occupying the interdendritic region. It has been shown that the solidification behavior of reverted alloys is different from that of virgin alloys [44,45]. This affects grain size, MC carbide size and morphology and the microporosity level.

The change in morphology of MC type carbide is one of the significant differences between reverted and virgin alloys. MC type carbide, which has FCC structure, is a primary carbide that usually forms from simple combination of carbon with reactive or refractory metals during solidification. M atoms are TiC, NbC, TaC, or HfC depending upon the composition of the alloy and can substitute for each other.

The MC carbide of a reverted alloy usually exhibits relatively small, blocky type morphology [44,47-49] rather than having Chinese script or mixed blocky/Chinese script form found in virgin alloy. Figure 3.11 [44] shows carbide morphology of Chinese script and blocky types, and Figure 3.12 [45] illustrates comparison of carbide shape distributions. Quested et al [49] have demonstrated that there is a transition in carbide morphology from a Chinese script to a blocky form as the solidification rate decreases in virgin alloys.

It is reported [13,47,49] that a region with a strong aluminum or titanium concentration is often found in blocky MC carbide as a nucleus. It is, therefore, suggested that highly reactive elements such as titanium and aluminum react with either nitrogen or oxygen to form very stable TiN, Ti(C,N) or $\text{Al}_2\text{O}_3$ particles in the melt before or during
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Figure 3.11 MC carbide morphology in virgin and reverted IN100 [44].

Figure 3.12 Comparison of carbide shape distribution. Shape factor Sc/P² is 0 for ideally thin carbides, and 0.0796 for perfectly round ones [45].
solidification which promote the heterogeneous nucleation of MC carbides in the reverted alloy. In addition to this, it is shown that some of the carbides in the revert have unusually high Ti and low Mo contents.

From the viewpoint of carbide morphology, Chinese script type MC carbides are preferable to blocky ones. The literature suggests that high nitrogen content turns carbide morphology into blocky, so it would be expected that Chinese script type is obtained if the nitrogen in the reverted alloy has been removed to appropriate level.

The other significant change in microstructure of the reverted alloy is an increase of microporosity [50-54]. In principle, microporosity can arise from shrinkage and gas evolution during solidification. In the case of superalloy, however, it must be noted that the gas contents such as nitrogen, oxygen and hydrogen are kept low and that most of them are either chemically bonded or kept in solution. It can then be assumed that microporosity formation is derived from solidification shrinkage. This shrinkage takes place when efficient liquid and mass feeding mechanisms are operative. However, since superalloys usually solidify in a mushy manner, mass feeding stops and capillary feeding, i.e., interdendritic feeding, becomes the only operative mode when about 70% of the alloy is solidified. Microporosity formation occurs during the last stage of solidification when capillary feeding becomes insufficient. In the case of reverted alloys whose nitrogen level is high, it will be expected that relatively large blocky carbides obstruct the feeding of the residual liquid into interdendritic region.

Microporosity formation can be formalized in terms of pressure. The formation can take place when the local pressure of the liquid metal, $P_L$, becomes smaller than the sum of three terms:
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\[ P_L \leq P_0 + P_m - \Delta P \]  \hspace{1cm} (3.4)

where \( P_0 \) and \( P_m \) are the external and the metallostatic pressure respectively, and \( \Delta P \) is the pressure drop associated with the liquid metal flow through the mushy zone. As solidification proceeds, \( \Delta P \) continuously increases and the local pressure \( P_L \) may eventually become negative. The parameter for microporosity formation, \( \Delta P \), is expressed as a function of solidification conditions, such as flow velocity, viscosity of the liquid, permeability, the volume fraction of the liquid, etc.

Lecomte-Beckers et al. [50,51] demonstrated that the tendency to microporosity formation in superalloys can be predicted by a microporosity index \( \Delta P^* \), which is formulated as:

\[
\Delta P^* = \frac{24\mu (\rho_S - \rho_L) n \tau^3}{\rho_L^2 \cdot g} \left( \frac{\Delta T}{G} \right)^2 \left( \frac{df_s}{dt} \right)
\]  \hspace{1cm} (3.5)

where \( \mu \) is the viscosity of interdendritic liquid, \( \rho_S \) and \( \rho_L \) are the densities of the solid and liquid respectively, \( (\rho_S - \rho_L)/\rho_L \) represents the solidification shrinkage, \( n \) is the number of interdendritic channels per unit area, \( \tau \) is the tortuosity of the dendrites, \( g \) is the gravity constant, \( \Delta T \) is solidification range, \( G \) is thermal gradient in the mushy zone, and \( (df_s/dt) \) is the average solidification rate at the end of solidification.

It has been reported [44,47] that the number of microporosities is a function of the nitrogen content, as shown in Figure 3.13. It can then be assumed that nitrogen in the alloy, consequently forms nitride, affect solidification parameters represented in equation (3.5).
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Figure 3.13 Relationship between microporosity and nitrogen content for IN100 heats [44].
3.3.3. Solidification Behavior

The difference in solidification behavior of the reverted alloys has been extensively studied by many researchers [46,47,50-57] in conjunction with microporosity formation. They examined the solidification sequence by using differential thermal analysis (DTA) and directionally solidified and quench (QDS) method [53,58].

The most significant difference between virgin and reverted alloy is the change of the total heat of solidification. The comparisons reported have shown that total heat of solidification is approximately 10% lower for a VIM revert melt than a VIM virgin melt, i.e., 90 cal/g for a revert and 100 cal/g for a virgin [44,45] in case of IN100, and about 50% lower in case of IN713C [57]. The difference of total heat of solidification affects the fraction solidified, \( f_s \), in the mushy zone during freezing. Figure 3.14 [46] indicates the fraction solidified of IN100 and Mar-M002 (which contains 1.5% hafnium and is a derivative of Mar-M247). There is no significant difference in the fraction solidified for Mar-M002, however, the solidification is more advanced for the revert than the virgin alloy in the case of IN100. All the curves shown in Figure 3.14 exhibit a kink at the onset of MC carbide precipitation, and MC carbides in reverted IN100 are considered to precipitate at lower temperature than in virgin.

The reason for the difference of the lower heat of solidification is explained by the existence of nuclei in the revert. It is suggested earlier that the revert contains higher level of nitrogen and that nitrides can act as nuclei for MC carbide formation. Since MC carbides precipitate heterogeneously on the nitride nuclei in the revert, it is expected that less energy is required to overcome the nucleation energy barrier of carbide formation. This finding, however, is somewhat curious since the initial and final states of the alloy studied are the same.
Figure 3.14 Fraction solidified $f_s$ as a function of temperature for virgin and revert alloys. 
a) IN100: 9 ppm nitrogen in virgin and 17 ppm in revert, b) Mar-M002: 6 ppm in virgin and 15 ppm in revert [46]. The relative uncertainty of fraction is about 10%.
In the case of reverted alloy, the residual liquid in the mushy zone becomes cooler than in virgin alloy because of lesser heat generation by the exothermic carbide precipitation. The cooler liquid results in less fluidity and less permeability. Microporosity may form at a point when the pressure drop associated to the viscous flow in the mushy zone, $\Delta P$, exceeds a critical value. The pressure drop can be calculated for porous media where the local gradient of pressure drop is a function of the local flow velocity, $\bar{V}$ [59,60]:

$$\bar{\text{Grad}} \Delta P = -\frac{\mu}{K} \bar{V}$$

where $\mu$ is the viscosity of the liquid and the permeability $K$ is related to the morphological characteristics, the volume fraction of liquid $f_l$ and the specific area of liquid/solid interface $\sigma$.

$$K = \alpha \frac{f_l^3}{\sigma^2} = \alpha \frac{(1-f_s)^3}{\sigma^2}$$

It is obvious from equation (3.7) that the permeability of the liquid of reverted alloy is lower than that of virgin alloy due to higher $f_s$ and $\sigma$ of the reverted liquid. Therefore, it becomes more difficult for the less-fluid residual liquid to feed into interdendritic solidification shrinkage. As a consequence, a greater number of microporosities form in the reverted alloy.

The results of DTA analysis have shown that there is no noticeable effect of nitrogen on characteristic temperatures of the alloy such as liquidus temperature, carbide formation temperature and eutectic temperature. Table 3.5 lists characteristic temperatures of the solidification sequence for IN100 and Mar-M002 [46]. It is shown that the characteristic temperatures of several heats of the reverted and virgin alloys are within the range of small variations that are caused by variations in the alloy composition. These characteristic temperatures show good agreement with other published results [61].
Table 3.5 Characteristic temperatures of the solidification sequence of IN100 and Mar-M002. $T_L$, liquidus temperature; $T_C$, MC carbide formation temperature; $T_B$, $\gamma$-$\gamma'$ eutectic formation temperature [46].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>IN100</th>
<th>Mar-M002</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l \rightarrow \gamma$</td>
<td>$T_L$</td>
<td>1322 – 1333</td>
</tr>
<tr>
<td>$l \rightarrow \gamma + \text{MC}$</td>
<td>$T_C$</td>
<td>1300 – 1310</td>
</tr>
<tr>
<td>$l \rightarrow \gamma + \gamma'$</td>
<td>$T_B$</td>
<td>1250</td>
</tr>
</tbody>
</table>
3.4. Formation of Titanium Nitride

Titanium nitride (TiN) is well known as a stable compound at high temperature. It has FCC (B1) structure, melting point of 2950 ± 50 °C and density of 5.21 g/cm³. In the case of recycling of superalloys, TiN particles either pre-exist in the scrap material or precipitate before or during solidification due to higher nitrogen content in the melt. The formation of TiN is controlled by the solubility product of TiN.

3.4.1. Solubility of Nitrogen

The solubility of nitrogen in superalloys is usually higher than in steels due to significant contents of reactive elements such as titanium and chromium. Similarly in steels, it is the fact that solubility of nitrogen in superalloys obeys Sievert's law, i.e., solubility of nitrogen can be determined by the nitrogen partial pressure, \( P_{N_2} \), under an equilibrium condition.

3.4.1.1. Thermochemical Consideration

The solution of nitrogen into nickel liquid is expressed by the reaction:

\[
\frac{1}{2} \text{N}_2(g) = \text{N}, \quad \text{for which the equilibrium constant } \quad K_N = \frac{a_N}{\sqrt{P_{N_2}}} \tag{3.8}
\]

where \( a_N \) is the activity of nitrogen, \( a_N = [\text{wt.} \% \text{N}] f_N \), and \( f_N \) is Henrian activity coefficient. The activity \( a_N \) and activity coefficient \( f_N \) are defined as:

\[
\lim_{\text{wt.} \% \text{N} \to 0} [\text{wt.} \% \text{N}] = a_N \quad \text{and} \quad \lim_{\text{wt.} \% \text{N} \to 0} f_N = 1 \tag{3.9}
\]

For infinitely dilute solution, i.e., \( f_N = 1 \), the equilibrium constant for nitrogen solution is:
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\[
K_N = \frac{[\text{wt.} \text{%} N] \cdot f_N}{\sqrt{P_{N_2}}}
\]  \hspace{1cm} (3.10)

\[
[\text{wt.} \text{%} N]_{Ni} = K \sqrt{P_{N_2}}
\]  \hspace{1cm} (3.11)

Wada et al. [62] experimentally determined the standard free energy for nitrogen solution in nickel liquid:

\[
\Delta G_N^o = 8250 + 8.84T \text{ (cal/g-atom)} \text{ at 1 atm } N_2
\]

\[
\log K_N = -\frac{1803}{T} - 1.93
\]  \hspace{1cm} (3.12)

Therefore, the solubility of nitrogen in pure nickel is obtained by following equation.

\[
\log[\text{wt.} \text{%} N]_{Ni} = \left(-\frac{1803}{T} - 1.93\right) + \frac{1}{2} \log\left(P_{N_2}\right)
\]  \hspace{1cm} (3.13)

In practice, it has been reported [62-65] that the solubility of nitrogen in nickel liquid is 13 ~ 20 ppm at 1600 °C and a nitrogen partial pressure of 1 atm.

In the case of nickel base alloys, the solubility of nitrogen has a following relationship:

\[
f_N = \frac{[\text{wt.} \text{%} N]_{Ni}}{[\text{wt.} \text{%} N]_{alloy}}|_{P_{N_2}, T}
\]  \hspace{1cm} (3.14)

where the activity coefficient of nitrogen \(f_N\) is defined as:

\[
\log f_N = \sum_j \epsilon_N^{j}[\text{wt.} \text{%} j]
\]

\(\epsilon_N^{j}\) is the interaction coefficient of component \(j\) for nitrogen in pure nickel.

Hence, the solubility of nitrogen in the alloy is expressed by:

\[
\log[\text{wt.} \text{%} N]_{alloy} = \log[\text{wt.} \text{%} N]_{Ni} - \log f_N
\]  \hspace{1cm} (3.15)
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The interaction coefficients of the elements, $e_{ij}$, in liquid nickel were experimentally determined and were noted in the literature [64, 66-68]. Table 3.6 summarizes the first order interaction coefficients for the elements contained in nickel base alloys.

Chipman and Corrigan [69] developed an equation for calculating the nitrogen solubility in molten steel dealing with $f_N$ as a function of temperature as indicated in Figure 3.15.

$$\log[\text{wt.%N}]_{\text{alloy}} = \log[\text{wt.%N}]_{\text{pure metal}} - \left(a + \frac{b}{T}\right) \sum e_{ij}^{1873K} \text{[wt.%j]}.$$  \hspace{1cm} (3.16)

$a = -0.75$ and $b = 3280$.

It can be predicted that the interaction coefficients in nickel melt will behave in the same manner as in steel melt. Mitchell has reported the solubility of nitrogen in five nickel base alloys melted under constant vacuum [70]. Figure 3.16 shows that the solubility of nitrogen depends on alloy compositions and the temperature of the alloy melt and that it increases with increasing temperature. Using the data, equation (3.16) can be modified for nickel base alloys.

$$\log[\text{wt.%N}]_{\text{alloy}} = \log[\text{wt.%N}]_{\text{Ni}} - \left(4.50 - \frac{5580}{T}\right) \sum e_{ij}^{1873K} \text{[wt.%j]}.$$  \hspace{1cm} (3.17)

Using the first order interaction coefficients $e_{ij}^{Ni}$ listed in Table 3.6, the equation for the solubility of nitrogen in nickel base alloy melt is defined as:

$$\log[\text{wt.%N}]_{\text{alloy}} = \left(-\frac{1803}{T} - 1.93\right) + \frac{1}{2} \log(P_{N_2}) - \left(4.50 - \frac{5580}{T}\right)(-0.10\text{[wt.%Cr]})$$

$$- 0.005[\text{wt.%Co}] - 0.038[\text{wt.%Mo}] - 0.21[\text{wt.%Ti}] - 0.15[\text{wt.%V}]$$

$$- 0.022[\text{wt.%W}] - 0.075[\text{wt.%Nb}] - 0.020[\text{wt.%Fe}] - 0.23[\text{wt.%Zr}]$$  \hspace{1cm} (3.18)
Table 3.6 First order interaction coefficients for nitrogen in pure nickel at 1650 °C.

<table>
<thead>
<tr>
<th>$j$</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
<th>Al</th>
<th>V</th>
<th>W</th>
<th>Nb</th>
<th>Fe</th>
<th>Zr</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_N^j$</td>
<td>-0.005</td>
<td>-0.101</td>
<td>-0.038</td>
<td>-0.21</td>
<td>0</td>
<td>-0.15</td>
<td>-0.022</td>
<td>-0.075</td>
<td>-0.020</td>
<td>-0.23</td>
<td>0</td>
</tr>
<tr>
<td>ref.</td>
<td>[64]</td>
<td>[66]</td>
<td>[68]</td>
<td>[67]</td>
<td>[68]</td>
<td>[67]</td>
<td>[67]</td>
<td>[66]</td>
<td>[64]</td>
<td>[68]</td>
<td>[68]</td>
</tr>
</tbody>
</table>

Figure 3.15 Relationship between nitrogen solubility, temperature and the interaction coefficient in molten steel [69].
Figure 3.16 Solubility of nitrogen in several nickel base superalloys [70].
Nitrogen solubility in alloy SRR99

Nitrogen solubility in alloy AF115

Figure 3.16 Solubility of nitrogen in several nickel base superalloys [70]. (continued)
3.4.1.2. Estimation of Solubility of Nitrogen

From equation (3.18), it is calculated that the solubility of nitrogen of virgin IN100 at the liquidus temperature (1330 °C) is 3 ~ 20 ppm under the nitrogen partial pressure ranging from $10^{-6}$ to $10^{-4}$ atm, which is the typical pressure range for VIM processes. The dependence on $N_2$ partial pressure and temperature calculated from equation (3.18) is shown in Figure 3.17.

In practice, the nitrogen contents of VIM processed IN100 are in the range of 4 ~ 12 ppm [44-46,56]. While the practical data are from both commercially and experimentally VIM processed heats, the nitrogen levels among the heats do not have any difference. It can be stated that the solubility of nitrogen calculated from equation (3.18) shows good agreement with the nitrogen levels in practical VIM heats.

3.4.2. Formation of Titanium Nitride

3.4.2.1. Thermochemical Consideration

During melting and solidification, the TiN precipitation is controlled by its solubility product. The essential reaction and the equilibrium constant of TiN precipitation are:

$$\text{TiN}(s) = \text{Ti} + \text{N}$$

(3.19)

and

$$K_{\text{TiN}} = \frac{a_{\text{Ti}} \cdot a_{\text{N}}}{a_{\text{TiN}}} = a_{\text{Ti}} \cdot a_{\text{N}} = f_{\text{Ti}}[\%\text{Ti}] \cdot f_{\text{N}}[\%\text{N}]$$

(3.20)

where $a_i$ and $f_i$ are the activity and the activity coefficient of component i, respectively. This reaction has a temperature dependence such that the equilibrium moves to the right side.
Figure 3.17 Dependence of the solubility of nitrogen in IN100 on nitrogen partial pressure and temperature, calculated by equation (3.18).
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with increasing temperature. Equation (3.20) shows that the reaction also has a composition dependence, controlled by the activity coefficients and contents of titanium and nitrogen (Figure 3.18 [13]). The primary factors in the composition dependence are the analytical contents of two components.

The standard free energy of the reaction (3.19) will be calculated from the standard free energy changes for following reactions.

\[ \text{TiN}(s) = \text{Ti}(s) + \frac{1}{2} \text{N}_2(g), \quad \Delta G^\circ = 84080 - 24.19T \text{ (cal/g-atom)} \] (3.21)

\[ \frac{1}{2} \text{N}_2(g) = \text{N}, \quad \Delta G^\circ = 8250 + 8.84T \text{ (cal/g-atom)} \] (3.22)

\[ \text{Ti}(s) = \text{Ti}, \quad \Delta G^\circ = -28300 - 10.66T \text{ (cal/g-atom)} \] (3.23)

From equation (3.19) through (3.23), the standard free energy change for TiN precipitation is obtained as:

\[ \Delta G_{\text{TIN}}^\circ = 64030 - 26.01T \text{ (cal/g-atom)} \] (3.24)

From equation (3.20),

\[ \log K_{\text{TIN}} = \log K_{\text{TIN}}^\circ + \log f_{\text{Ti}} + \log f_{\text{N}} \]

\[ \log K_{\text{TIN}}^\circ = \log [\text{wt.}%\text{Ti}][\text{wt.}%\text{N}] = \log K_{\text{TIN}} - \log f_{\text{Ti}} - \log f_{\text{N}} \] (3.25)

The equilibrium constant \( K_{\text{TIN}} \) can be calculated from the standard free energy for TiN formation, \( \Delta G_{\text{TIN}}^\circ \).

Using the relationship, \( \Delta G_{\text{TIN}}^\circ = -RT \ln K_{\text{TIN}} \), and equation (3.24),

\[ \log K_{\text{TIN}} = -\frac{13995}{T} + 5.69. \] (3.26)

The activity coefficient for nitrogen, \( \log f_{\text{N}} \), can be calculated by the third term of right hand side of the equation (3.18). The activity coefficient for titanium, \( \log f_{\text{Ti}} \), can also be
Figure 3.18 Temperature and composition dependence of saturation solubility of TiN in IN718 [13].
obtained the same manner as \( \log f_{N} \). Therefore, \( \log f_{Ti} \) is simply expressed the sum of the interaction coefficients of the component \( i \) for titanium in nickel liquid.

\[
\log f_{Ti} = \sum_{i} e_{Ti}^{i} [\text{wt.}\% i]
\]  

(3.27)

or the form that temperature dependence is taken into account is:

\[
\log f_{Ti} = \left( \frac{a}{T} + b \right) \sum_{i} e_{Ti}^{i} 1873K [\text{wt.}\% i]
\]  

(3.28)

However, only few interaction coefficients for titanium in the liquid nickel can be available in the literature, as shown in Table 3.7 [68]. In \( \log f_{Ti} = \sum_{i} e_{Ti}^{i} [\text{wt.}\% i] \), the two terms, \( e_{Ti}^{O} [\text{wt.}\% O] \) and \( e_{Ti}^{S} [\text{wt.}\% S] \), are so small that they can be negligible because oxygen and sulfur contents in superalloys are usually very low, e.g., \( O = 10 \) ppm and \( S = 3 \) ppm. Then dominant factors of \( \log f_{Ti} \) are \( e_{Ti}^{C} [\text{wt.}\% C] \) and \( e_{Ti}^{Ti} [\text{wt.}\% Ti] \).

The solubility product of TiN in nickel base alloys also has a strong dependence on chromium content of the alloy while it seems to be controlled by the factors: the activity coefficients and contents of titanium and nitrogen. Mitchell [70] has reported that chromium strongly affects the activity of nitrogen and the solubility products of TiN in superalloys consequently show strong dependence on chromium contents (Figure 3.19).

It can also be predicted from his results that the dependence of the solubility product on chromium content is maintained at least up to the temperature of \( T_{\text{liquidus}} + 60^\circ C \). In this temperature range, the solubility products for several nickel base alloys he examined (the nominal compositions of these alloys are listed in Appendix A) are:
Table 3.7 First order interaction coefficients for titanium in pure nickel at 1600 °C [68].

<table>
<thead>
<tr>
<th>i</th>
<th>C</th>
<th>S</th>
<th>Ti</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_i^{T_i}$</td>
<td>-0.101</td>
<td>0.237</td>
<td>0.08</td>
<td>-1.536</td>
</tr>
</tbody>
</table>

Figure 3.19 Dependence of solubility product of TiN on chromium content [70].
3.4.2.2. Effect of Segregation on Titanium Nitride Precipitation

The segregation of the components during solidification is a principal characteristic of multi-component alloys, i.e., superalloys. The solidification sequence of superalloy is complex and the concentration of the elements can be greatly enhanced over the bulk concentration. In order to estimate the TiN precipitation, therefore, not only the temperature dependence of the solubility product but also the change in element concentration in the interdendritic liquid must be taken into account.

Cockcroft et al. [13] have reported the effect of titanium segregation on TiN precipitation in IN718. They calculated titanium segregation taken place on freezing from the relationship between the fraction solidified and temperature and the Scheil equation:

\[
C_1 = C_0 (1 - f_s)^{k_0}^{-1}
\]  

(3.29)

where \( C_0 \) and \( C_1 \) are the initial concentration and the concentration in the solid of the element, respectively. \( f_s \) is the fraction solidified, and \( k_0 \) is the segregation coefficient. Figure 3.20 shows the result of calculation. This demonstrates that the titanium concentration has risen to about 4 wt.% at the temperature of an initiation of primary NbC carbide precipitation, i.e., 1280 – 1290 °C.
Assuming that the solubility of nitrogen is not affected by segregation, it is concluded that the solubility of nitrogen is reduced to about 1 ppm at around 1290 °C and that the segregation combined with temperature change enhances TiN precipitation. Almost all of nitrogen saturated in the liquid at the liquidus temperature is consumed to precipitate TiN particles before the MC carbide precipitation takes place. The evidence is indicated in Figure 3.21 [13] in which the structure of "carbonitride" in IN718 is shown. In the carbonitride, MgO-Al2O3 core (the hexagonal faceting) surrounded by TiN acts as the nucleus for a primary MC carbide (NbC).

Since the density of TiN is significantly smaller than that of the liquid IN718, it is possible that the buoyancy forces might cause it to escape from the solidifying matrix. It can be implied that it might be possible to remove the TiN particles from the melt if sufficient time for TiN particle to float up to the liquid surface is given.

### 3.4.2.3 Estimation of Solubility Product of Titanium Nitride

The solubility product of TiN in IN100 may be estimated by using equation (3.25). Assuming that the effect of temperature on logfTi is small, it can be calculated for IN100 that logfTi = 0.365 from equation (3.27) and eTi values. The term, logfN, can be calculated from the third term of right hand side in equation (3.18) and logfN = -2.40 at 1330 °C. Therefore the solubility product of TiN for IN100 at the liquidus temperature can be estimated as:

\[ K'_{\text{TIN}} = 9.9 \times 10^{-2}. \]  

(3.30)

Since nominal content of titanium in IN100 is 4.75 wt. %, the nitrogen limit for TiN formation at the liquidus temperature is obtained from (3.30):

\[ [\text{wt.}\%\text{N}] = 0.020 \text{ at 1330 °C}. \]
Figure 3.20 Relationship between temperature, fraction solidified and segregation of titanium during the freezing of IN718 [13].

Figure 3.21 Precipitation structure of "carbonitride" in IN718, showing an MgO-Al₂O₃ core (note the hexagonal faceting) surrounded by TiN, which acted as the nucleant for a primary MC carbide (lighter-colored coating on the TiN crystal) [13].
However, it is the fact that TiN particles are found in reverted IN100 in which nitrogen content is about 20 ppm [44,57]. The estimated value of $K'_{\text{TiN}}$ here is an order of magnitude larger than a predictable value in practice. It is considered that the reason for such disagreement between both $K'_{\text{TiN}}$ values is due to uncertainty of the interaction coefficients for titanium.

Another way to estimate the solubility product of TiN is to use its dependence of chromium content as shown in Figure 3.19. Applying this relationship for the case of IN100 that contains 10.0 wt.% chromium and 4.75 wt.% titanium, the estimated solubility product of TiN at a given temperature can be approximately estimated by following equation:

$$\log K'_{\text{TiN}} = -\frac{10390}{T} + 3.87$$

(3.31)

The nitrogen limit for TiN formation at given temperature can be calculated from

$$\log(K' = \log(\text{wt.}%\text{Ti})\times\log(\text{wt.}%\text{N})$$

$$\log(\text{wt.}%\text{N}) = -\frac{10390}{T} + 3.20$$

(3.32)

At the liquidus temperature of IN100 (1330 °C),

$$[\text{wt.}%\text{N}] = 5.2 \times 10^{-4}$$

The nitrogen limit estimated is about 5 ppm at the liquidus temperature of IN100 and this seems to be reasonable. This will be a critical value of nitrogen content for TiN formation in IN100. In other words, any TiN particle will not form at the liquidus temperature if the nitrogen content is less than the critical value of nitrogen.

The factor taken into account for the estimation of the solubility product of TiN is the segregation of titanium during solidification. The segregation can be predict from the Scheil equation (3.29). In this equation, the segregation coefficient $k_0$ is obtained by the
From Ni-Ti phase diagram (Figure 3.22 [73]), the segregation coefficient of titanium is estimated as:

\[ k_0 = 0.70 \]

In the case of IN100, the initial concentration of titanium in the liquid \( C_0 \) is 4.75 wt.%. Therefore the solid concentration \( C_1 \) can be calculated by:

\[ C_1 = 4.75 \cdot (1 - f_s)^{-0.30} \]  \hspace{1cm} (3.33)

Figure 3.23 shows the segregation of titanium during freezing in IN100 calculated from equation (3.33) and the fraction solidified during solidification (Figure 3.14). At about 1310 °C at which MC carbide precipitates, titanium concentration in the residual liquid will rise up to about 5.7 wt.%. 

Assuming that the relationship for the solubility product of TiN estimated as equation (3.31) is maintained within a temperature range of solidification, the nitrogen limit for TiN formation will be reduced by increase of titanium content due to its segregation. The solubility product of TiN in IN100 affected by titanium segregation is shown in Figure 3.24.

It is clear that the nitrogen limit for TiN formation is reduced from 5.2 ppm at 1330 °C to 3.5 ppm at 1310 °C by the segregation of titanium. If the nitrogen content of the alloy is less than 3.5 ppm, the precipitation of TiN that may affect MC carbide formation at around 1310 °C can be avoided.
Figure 3.22 Ni-Ti phase diagram [73].
Figure 3.23 The segregation of titanium in IN100 during solidification calculated by equation (3.33). Data of fraction solidified were taken from the literature [46].
Figure 3.24 Effect of titanium segregation on the solubility product of TiN in IN100.
3.5. Formation of Hafnium Oxide

Since hafnium is the element that has very strong affinity to oxygen, hafnium oxide (HfO$_2$) forms easily even under the situation in which other reactive elements such as aluminum and titanium co-exist. HfO$_2$ is very stable compound at elevated temperature. It transforms from monoclinic to tetragonal structure at about 1630 °C and from tetragonal to cubic structure at about 2700 °C. Cubic HfO$_2$ has high melting point of $2900 \pm 25$ °C. The density of HfO$_2$ is 10.3 g/cm$^3$, i.e., significantly greater than that of a superalloy melt, e.g., 8.0 g/cm$^3$.

In the case of hafnium-bearing superalloys, two possible reasons of HfO$_2$ formation can be considered:

(1) those which precipitate by combining resolved oxygen in the melt during melting or solidification.

(2) those which react with oxide, refractory crucible in most case, during processing of the alloy [74].

In the case of recycling of the scrap that probably contains HfO$_2$ particle as an inclusion, the source of such a pre-existing HfO$_2$ particle may attribute its formation to either (1) or (2).

3.5.1. Precipitation of Hafnium Oxide

While superalloy contains relatively large amount of reactive elements such as chromium, aluminum and titanium, hafnium has a strong reactivity with oxygen. It is therefore expected that hafnium forms HfO$_2$ when there is a sufficient oxygen in the melt to react.

The essential reaction for the precipitation of HfO$_2$ in liquid nickel is expressed as:
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\[ \text{HfO}_2 (s) = \text{Hf} + 2\text{O} \] \hspace{1cm} (3.34)

The standard free energy change for the reaction can be calculated from the following reactions.

\[ \text{HfO}_2 (s) = \text{Hf} (s) + \text{O}_2 (g) , \quad \Delta G^\circ = 253930 - 41.58T \text{ (cal/g-atm)} \{66\} \hspace{1cm} (3.35) \]

\[ \text{Hf} (s) = \text{Hf}^0 , \quad \Delta G^\circ = -61210 - 0.25T \text{ (cal/g-atm)} \{75\} \hspace{1cm} (3.36) \]

\[ \frac{1}{2} \text{O}_2 (g) = \text{O} , \quad \Delta G^\circ = -19050 + 1.71T \text{ (cal/g-atm)} \{76\} \hspace{1cm} (3.37) \]

From equation (3.36) through (3.38), the standard free energy change and the equilibrium constant for reaction (3.34) are:

\[ \Delta G^\circ(3.34) = 154620 - 38.41T \text{ (cal/g-atm)} \] \hspace{1cm} (3.38)

\[ \log K(3.34) = \frac{-33795}{T} + 8.40 \] \hspace{1cm} (3.39)

The equilibrium constant \( K(3.34) \) is expressed by the activities, \( a_{\text{Hf}} \) and \( a_{\text{O}} \), and the activity coefficients, \( f_{\text{Hf}} \) and \( f_{\text{O}} \) of hafnium and oxygen. Suppose that standard state for HfO\(_2\) is a pure HfO\(_2\) solid, i.e., \( a_{\text{HfO}_2} \) the equilibrium constant \( K(3.34) \) is:

\[ K(3.34) = \frac{a_{\text{Hf}} \cdot a_{\text{O}}^2}{a_{\text{HfO}_2}} = f_{\text{Hf}}[\text{wt. %Hf}] \cdot f_{\text{O}}^2[\text{wt. %O}]^2 \] \hspace{1cm} (3.40)

The solubility product of HfO\(_2\) is expressed by the equation:

\[ \log K'(3.34) = \log[\text{wt. %Hf}][\text{wt. %O}]^2 \]
\[ = \log K(3.34) - \log f_{\text{Hf}} - 2 \log f_{\text{O}} \] \hspace{1cm} (3.41)

where the activity coefficients \( \log f_{\text{O}} = \sum_j e^j_{\text{O}} [\text{wt. %} j] \) and \( \log f_{\text{Hf}} = \sum_i e^i_{\text{Hf}} [\text{wt. %} i] \). The terms \( e^i_{\text{Hf}} \) and \( e^j_{\text{O}} \) are the first order interaction coefficients of component \( i \) for hafnium and of component \( j \) for oxygen, respectively.
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Ban-ya et al. [75] have determined the equilibria between hafnium and oxygen in liquid nickel, and they suggested that the solubility product of HfO$_2$, $\log K_{(3.34)}$, becomes:

$$\log K'_{(3.34)} = \log K_{(3.34)} - e^0_\text{O} (2[\text{wt.\%Hf}] + 11.15[\text{wt.\%O}])$$

where $e^0_\text{O} = 0$ [77] and $e^0_\text{Hf} = \frac{M_\text{Hf}}{M_\text{O}} e^H_\text{Hf} = 11.15 e^H_\text{O}$. While the value of $e^H_\text{Hf}$ in nickel is not clearly known, they assumed $e^H_\text{Hf} = 1$ for the calculation. Their result can only be applied for the condition at which hafnium content is up to 0.1 wt.% and which the temperature ranges from 1600°C to 1750°C. Figure 3.25 shows the relationship between the solubility product, $\log K'_{(3.34)}$, and $2[\text{wt.\%Hf}] + 11.15[\text{wt.\%O}]$ under the condition stated above [78]. Figure 3.26 shows the deoxidation equilibria in iron and nickel liquid [75]. As can be seen in the figure, the equilibria exhibit minima at 0.04 wt.% of hafnium content in iron and at 0.02 wt.% in nickel.

In most cases of cast nickel base alloys, hafnium contents are ranging from 1.4 wt.% to 2 wt.%. However, the equilibria of which hafnium content exceeds about 0.1 wt.% is not well-known. It is shown in Figure 3.26 that the equilibria in both iron and nickel can be divided into two regions: a region I in which oxygen content decreases to the minimum and increases with increasing hafnium content up to 0.1 wt.%, and a region II in which it seems to decrease again when hafnium content increases over about 0.1 wt.%. It is suggested that the reason for an existence of two regions is due to the difference in equilibrium phases. It is obvious that HfO$_2$ is the equilibrium phase in a region I. However, the phase in a region II is not clearly understood and it is expected [75] that lower oxides (e.g., HfO$_x$) or non-stoichiometric Hf-O solid solution may form.

In superalloys, the large amount of other elements such as aluminum and titanium that affect the activity of oxygen are contained. The solubility product of HfO$_2$ in the case of superalloys will be estimated by equation (3.41) and the relationships,
Figure 3.25 Plot of log $K_{\text{HfO}_2}$ vs. $2(\text{wt.}\%\text{Hf}) + \text{11.15[wt.}\%\text{O}]$ [78].

Figure 3.26 Relation between hafnium and oxygen contents a) in liquid iron and b) in liquid nickel [75].
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\[ \log f_0 = \sum_j e'_0 \ [\text{wt.} \% j] \text{ and } \log f_{\text{HF}} = \sum_i e'_{\text{HF}} \ [\text{wt.} \% i]. \]

The first order interaction coefficients of the elements for oxygen in liquid nickel are compiled in [63]. They are listed in Table 3.8.

On the other hand, however, there has not been any available data of the interaction coefficients for hafnium in nickel liquid. It is therefore difficult to estimate the solubility product of HfO\(_2\) in nickel base alloys due to lack of the data interaction coefficients.

Assuming that hafnium in nickel takes the same behavior as titanium, the solubility product of HfO\(_2\), \(K'_{(3,34)}\), in Mar-M247 will calculated using available thermochemical data as:

\[ \log K'_{(3,34)} = \log[\text{wt.} \% \text{Hf}] \left[ \text{wt.} \% \text{O} \right]^2 = -1.34 \text{ at } 1600 \, ^\circ\text{C}. \]

It is assumed that oxygen limit in this alloy, which contains 1.4 wt.% hafnium, at 1600 \(^\circ\)C becomes:

\[ [\text{wt.} \% \text{O}] = 320 \text{ ppm}. \]

In practical sense, however, the obtained value for oxygen limit seems to be large. Since oxygen contents of most of nickel base alloys for aerospace applications are about 10 ppm or less, it may be expected that oxygen limit is less than few ppm.

The other estimation of the saturation solubility of HfO\(_2\) is obtainable from extrapolation of the equilibrium in liquid nickel shown in Figure 3.26 b). Oxygen limit can be estimated as about 0.3 ppm at 1600 \(^\circ\)C. The estimated oxygen level seems to be reasonable and it should be lowered at liquidus temperature. It is therefore expected that all of the oxygen in the alloy would exist as HfO\(_2\) particles.
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Table 3.8  First order interaction coefficients for oxygen in nickel liquid at 1600°C [68].

<table>
<thead>
<tr>
<th>j</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>Al</th>
<th>Ti</th>
<th>V</th>
<th>Fe</th>
<th>Hf</th>
<th>C</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon^I_O$</td>
<td>-0.231</td>
<td>-0.004</td>
<td>-0.024</td>
<td>-1.058</td>
<td>-0.51</td>
<td>-0.40</td>
<td>-0.025</td>
<td>-9.75</td>
<td>-1.10</td>
<td>-0.011</td>
</tr>
</tbody>
</table>
3.5.2. Reaction with Refractory

Superalloy, whether it is virgin or reverted alloy, is usually processed by VIM furnace as a primary melting method. Among the melting practices of superalloys, VIM process is the only one process that uses refractory crucible. This gives hafnium in the alloy melt a chance to react with oxide refractories.

Since MgO, Al₂O₃ and MgO·Al₂O₃ spinell are the common materials used for the refractories of VIM furnace, it may be considered that hafnium in the liquid will react with these oxides. The possible reactions are:

\[3Hf + 2Al₂O₃ (s) = 4Al + 3HfO₂ (s)\]  \hspace{1cm} (3.42)

and

\[Hf + 2MgO (s) = 2Mg (g) + HfO₂ (s)\]  \hspace{1cm} (3.43)

In the case of the reaction with Al₂O₃, the formation of HfO₂ can be estimated by calculation of the standard free energy change or the equilibrium constant for reaction (3.42). Following reactions and reaction (3.34) are considered as elemental reactions:

\[Al₂O₃ (s) = 2Al (l) + \frac{3}{2}O₂ (g) , \quad ΔG^o = 400957 - 76.55T \text{ (cal/g-atm)} \]  \hspace{1cm} [79]  \hspace{1cm} (3.44)

\[Al (l) = Al , \quad ΔG^o = -37000 - 4.61T \text{ (cal/g-atm)} \]  \hspace{1cm} [67]  \hspace{1cm} (3.45)

From these data, the standard free energy change and the equilibrium constant are obtained as:

\[ΔG^o_{(3.42)} = 75754 - 46.05T \text{ (cal/g-atm)} \quad \text{and} \quad \log K_{(3.42)} = \frac{-17688}{T} + 10.7 \]  \hspace{1cm} (3.46)

For example, at 1500°C that is a typical melting temperature of superalloys, the equilibrium constant calculated by equation (3.46) is

\[K_{(3.42)} = 5.3\]
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It is clear that HfO$_2$ can form by the reaction with Al$_2$O$_3$ during VIM processing, but that the extent of the reaction will be critically dependent on the activity coefficient of Hf which is unknown.

In other case of the reaction with MgO, the elemental reactions are considered as

\[
\text{MgO} \rightarrow \text{Mg} \left( g \right) + \frac{1}{2} \text{O}_2 \left( g \right),
\]

and reaction (3.44).

The standard free energy change can be obtained by using a following data and reaction (3.47).

\[
\Delta G^\circ = 181770 + 7.37T \log T - 75.76T \text{ (cal/g-atm)} [79]
\]

The standard free energy change for reaction (3.47) becomes:

\[
\Delta G^\circ = 164630 + 7.37T \log T - 75.42T \text{ (cal/g-atm)}
\]

Therefore, the standard free energy change and the equilibrium constant for reaction (3.43) may be calculated as:

\[
\Delta G^\circ_{(3,43)} = 174640 + 14.74T \log T - 112.43T \text{ (cal/g-atm)}
\]

and

\[
\log K_{(3,43)} = -\frac{38170}{T} - 3.22 \log T + 24.57
\]

In reaction (3.47), however, not only temperature dependence but also a vapor pressure of magnesium and the operating pressure of VIM must be taken into consideration. The equilibrium constant for reaction (3.43) is also expressed as a function of vapor pressure of magnesium.

\[
\log K'_{(3,43)} = \frac{R_{\text{Mg}} \cdot a_0}{a_{\text{MgO}}} = R_{\text{Mg}} \cdot a_0
\]
Since the standard vapor pressure of pure magnesium, $P_{Mg}^{o}$, can be defined [80] as:

$$\log P_{Mg}^{o} = -\frac{7780}{T} - 0.85 \log T + 11.41 \text{ (torr)} \quad \text{for solid element} \quad (3.52)$$

or

$$\log P_{Mg}^{o} = -\frac{7550}{T} - 1.41 \log T + 12.79 \text{ (torr)} \quad \text{for liquid element,} \quad (3.53)$$

the vapor pressure of magnesium, $P_{Mg}$, is determined by Raoult's law:

$$P_{Mg} = P_{Mg}^{o} \times \gamma_{Mg} \times N_{Mg} \quad (3.54)$$

where $\gamma_{Mg}$ is an activity coefficient of magnesium in solution in the alloy, and $N_{Mg}$ is a fraction of magnesium in solution.

It is readily predicted that the vapor pressure is so high at the melting temperature of superalloys. Addition to this, a vacuum level the alloy melt is encountered in a VIM furnace is relatively high, e.g., a level of $10^2$ atom. It is expected that the equilibrium of reaction (3.43) will move to the right, i.e., HfO$_2$ will form by the reaction with MgO.

It has been reported [39,41,81,82] that, in practice, oxygen levels of VIM processed hafnium-bearing superalloys such as Mar-M002, Mar-M247 and Rene 125 are approximately less than 10 ppm. Compositions of oxide inclusions contained in the alloys has been investigated by EB button technique and micro chemical analysis, and it is suggested [28,74,83] that major components of oxide inclusions are hafnium (HfO$_2$) and aluminum (Al$_2$O$_3$), that HfO$_2$ particles found on the raft area of EB button are essentially pure, i.e., >90% HfO$_2$ (Figure 3.27 [28]), and that almost all HfO$_2$ are considered to form by the reaction with refractories of the furnace or the casting mold [74] beacuse of relatively long contact time and considerable superheat especially in case of directional and single-crystal solidification.
Figure 3.27 Element distribution on a Rene 125 raft [28]. a) Backscattered image, b) Oxygen distribution, c) Hafnium distribution and d) aluminum distribution.
3.6. Summary

Among melting practices available for superalloys, whether they are primary or secondary processes, electron beam cold hearth remelting (EBCHR) method will be the most plausible for removal of inclusions such as TiN or HfO₂. It is expected that the mechanism employed for EB refining is principally separation due to the interfacial tension forces between the inclusion particles and the liquid surfaces, or alternatively due to the density differences between the particles and the melt. The former mechanism makes it possible that heavier inclusions than the melt may be retained on the liquid surface, whereas they will sink by the latter mechanism.

It was found that nitrogen in superalloys affects castability and microstructure of reverted superalloys by the precipitation of TiN. The increase in the number of microporosities and the change in MC carbide morphology are the major modifications in reverted superalloys. Those are considered to result from the lower heat of solidification of the melt due to heterogeneous precipitation of MC carbides on the TiN particles, although this finding is difficult to rationalize with the thermodynamic situation. In IN100 that has a relatively narrow solidification temperature range, the influences are clearly marked.

It becomes clear that solubility of nitrogen is dependent on the partial pressure of nitrogen and on temperature and that TiN precipitation is controlled by the solubility product which depends on the activities of titanium and nitrogen, i.e., concentrations of titanium and nitrogen and the melt temperature. It was estimated from thermochemical calculations that the solubility of nitrogen in liquid IN100 is about 10 ppm at the liquidus temperature, 1330 °C, under a nitrogen partial pressure of 10⁻⁵ torr, and that the solubility product of TiN, \( \log K'_{\text{TiN}} \), is -2.62. The nitrogen limit for the precipitation is about 5 ppm at the liquidus temperature for 4.7 wt.% of titanium in IN100.
Chapter 3 Literature Review

It can be suggested that removal of TiN from IN100 reverts will be accomplished by the flotation either due to relative density difference or due to interfacial tension forces since the particle is lighter than the melt.

For Hf-bearing superalloys that are mostly used for DS or single crystal turbine blades and are expensive, recycling of reverts is essential practice. In such superalloys, it is concluded that hafnium oxides (HfO₂) will predominantly form during melting, remelting and DS casting by the reaction with oxide refractories that contact the melt. It is obvious that decomposition of HfO₂ particle during remelting practices is impossible since it is a very stable compound. In order to remove such HfO₂ particles from reverts, the EBCHR process seems to be the most effective, in which the flotation due to the interfacial tension force will be a dominant mechanism of separation even though the density of HfO₂ particle is larger than that of the superalloy melt.
Chapter 4  Experimental Work

4. Experimental Work

4.1. Equipment

The major equipment used in this work consisted of a vacuum induction melting (VIM) furnace and an electron beam (EB) furnace. The VIM furnace has been designed for a study of directional solidification of superalloys. The EB furnace was used mainly for remelting of the alloys.

4.1.1. Vacuum Induction Melting Furnace

The VIM furnace consists of a vacuum system, a chamber and a crucible section. Figure 4.1 shows an overview and a schematic configuration of the VIM furnace. A diffusion pump and mechanical rotary pump are used for the vacuum system. The chamber can be divided into two sections: a lower chamber that is connected to the pumps through vacuum valves and that holds a water-cooled copper chill, and an upper chamber in which a crucible section is located.

The vacuum system consists of a diffusion pump backed by a mechanical pump. Both pumps are connected to the lower chamber through vacuum valves. During initial operation, the chamber is evacuated by the mechanical pump only. After the vacuum level reaches about 0.2 torr, the diffusion pump backed by mechanical pump is connected in series to the chamber. They can evacuate the chamber to approximately $10^{-6}$ torr. The lower chamber, in which a crucible and chill are contained, is isolated from the atmospheric
Figure 4.1 Overview and schematic configuration of the VIM furnace.
environment by a quartz glass tube. Both ends of quartz tube are sealed with metal-O-ring-glass contacts, tightened with metal screws.

An alumina crucible wrapped by Mo foil and surrounded by three alumina radiation shields is set on a water-cooled copper chill. A chill block made of steel is located between the water-cooled copper chill and molten alloy. Figure 4.2 illustrates the crucible section of the VIM furnace.

In operation, alloy blocks already cut and cleaned are charged into an alumina crucible. For this work, about 350 g of charge material was used for one heat. After the system is evacuated and the vacuum reaches steady state, i.e., $10^{-5} \sim 10^{-6}$ torr, electrical power, e.g., 11 kW, is applied for the induction coil to melt the charge material.

After the alloy stock becomes completely molten under vacuum, directional solidification is carried out by the reduction of the induction power to the melt, for example, the power is reduced to 4 kW. During solidification, heat is extracted downward from the water-cooled copper chill through steel chill block. Three alumina radiation shields that surround the crucible prevent loss of heat in the radial direction. As a result, a longitudinal thermal gradient is formed, and the solidification takes place directionally from the bottom to the top of the melt.

4.1.2. Electron Beam Furnace

The EB furnace consists of a 40 kW electron beam gun, a main chamber and two sets of vacuum systems; one is for the chamber and the other for the gun. An overview and a schematic drawing of the EB furnace is illustrated in Figure 4.3.
Figure 4.2 Schematic drawings of crucible section of VIM furnace.
Figure 4.3 Overview and schematic drawing of EB furnace.
Chapter 4 Experimental Work

Two sets of vacuum pumps of different capacities, diffusion pump and mechanical backup pump, are used for both the main chamber and the EB gun. They can obtain vacuum levels of approximately $10^{-6}$ torr for the main and gun chambers.

The EB gun consists of a filament, a cathode, an anode, and a beam deflection and scanning controller. The assembly is set in the gun chamber. Figure 4.4 shows a simplified EB gun configuration. The parts of the gun from which the electron beam is emitted are heating filament, cathode and anode. During operation, the cathode is being heated by bombardment from the filament. At the same time, high voltage is applied between cathode and anode as an acceleration potential for thermoelectrons. Thermal electrons are emitted from cathode, accelerated by the potential gradient, focused, controlled in direction and finally deposited on the target material. The position of the electron beam emitted from the gun is controlled by a deflection and scanning controller that is connected to a control panel. One can control the direction or scanning of the beam either manually or automatically by a computer.

Material to be melted is either located on an edge of the water-cooled copper mold if it is small or fed onto the mold by a charge feeder if relatively large. Liquid droplet formed by an electron beam falls into the mold, is kept molten for a while and finally freezes.

4.2. Material

4.2.1. Superalloy

Two kinds of superalloys were used for this project: IN100 for an investigation of TiN removal and Mar-M247 for HfO$_2$ removal. Both alloys were supplied as cast forms
Connect to power supply

![Diagram of EB gun configuration]

**Figure 4.4** Schematic configuration of EB gun.
from a superalloy producer, Cannon-Muskegon Corporation, and they were used as raw materials for this work. The chemical concentrations of the major elements in these alloys are listed in Table 4.1.

4.2.2. Additive

Ferro-chromium nitride powder was used for the investigation of TiN formation as a nitrogen source to IN100. It was supplied from Sanyo Special Steel Co., Ltd., and originally produced by Nippon Jyukagaku-kogyo Co., Ltd. Its chemical composition is shown in Table 4.2. Since the desired nitrogen content in IN100 is about 50 ppm, the increases in iron and chromium contents are 0.02 wt.% and 0.03 wt.% respectively. These increases are negligible.

4.3. Experimental Procedure

Directionally solidified cast samples were made using the VIM furnace. The EB furnace was used for the examination of the behavior of inclusions during melting and freezing.

4.3.1. Vacuum Induction Melting Furnace Operation

The following procedure was taken for VIM furnace operation in order to obtain directionally solidified cast samples.

1. Set the steel chill block onto the water-cooled copper chill.
2. Put the alloy stock prepared into the alumina crucible, and place them on the copper chill.
### Table 4.1 Chemical compositions of the alloys for this work.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>Al</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN100</td>
<td>9.9</td>
<td>15.0</td>
<td>3.26</td>
<td>----</td>
<td>----</td>
<td>5.46</td>
<td>4.45</td>
</tr>
<tr>
<td>Mar-M247</td>
<td>8.3</td>
<td>10.0</td>
<td>0.64</td>
<td>9.9</td>
<td>3.14</td>
<td>5.61</td>
<td>0.98</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>V</th>
<th>Hf</th>
<th>C</th>
<th>B</th>
<th>Zr</th>
<th>O (ppm)</th>
<th>N (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN100</td>
<td>0.97</td>
<td>----</td>
<td>0.168</td>
<td>0.015</td>
<td>0.05</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>Mar-M247</td>
<td>----</td>
<td>1.4</td>
<td>0.152</td>
<td>0.015</td>
<td>0.03</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

### Table 4.2 Chemical analysis of chromium nitride powder.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>N</th>
<th>Fe</th>
<th>C</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium nitride</td>
<td>58.9</td>
<td>6.28</td>
<td>34.01</td>
<td>0.005</td>
<td>0.0002</td>
</tr>
</tbody>
</table>
3. Position alumina radiation shields on the copper chill.
4. Close the upper part of the chamber. Make sure that seals are clean and all the valves are set properly.
5. Pump the system by mechanical pump until the vacuum reaches about 0.2 torr.
6. Switch the valve for the diffusion pump and wait until the vacuum reaches a steady state close to $10^{-6}$ torr (wait about one hour).
7. Gradually increase the power to the induction coil to the desired power level, e.g., 11 kW.
8. Reduce the power to solidify the melt, e.g., 4 kW, after the alloy becomes completely molten.
9. Power off after the melt entirely solidifies.
10. Wait about two hours until the cast becomes cool enough to handle.

4.3.2. Electron Beam Furnace Operation

The following procedure, with minor modification, was taken for the EB furnace operation in order to examine the behavior of inclusions during EB melting.

1. Place the sample on a edge of the wall of the copper mold if it is small, or fix to the charge feeder. Make sure that the water-cooled copper mold is clean.
2. Pump the chamber using mechanical pump until the vacuum reaches at least 0.2 torr.
3. Change the vacuum valve to the diffusion pump, backed up by mechanical pump, and after a while, pump the EB gun chamber.
4. Wait until the vacuum reaches a steady state, i.e., about $10^{-6}$ torr (wait about two hours).
5. Set the melting condition such as filament current, excitation voltage and beam voltage and current.
Chapter 4  Experimental Work

6. Control the direction of the beam with adjusting the beam power in order to melt the sample.

7. Wait for one to four hours, depending on the volume of the sample, until the sample becomes cool enough to handle.

4.4. Sample

Two types of samples were obtained: one was from the VIM furnace and the other was from the EB furnace. Samples made using the VIM furnace were directionally solidified cast samples that were provided for the observation of structures, qualitative and quantitative analysis. Some of them were used as the stocks for EB melting. Their typical dimensions were roughly 21 mm in diameter and 80 mm in length.

Two kinds of samples were obtained from EB melting operation. One was the frozen droplet sample and the other was the so-called EB button sample (Figure 4.5). The former was the one that the alloy liquid melted by electron beam fell down onto the water-cooled copper and solidified immediately. Inclusions retained on the liquid surface by surface tension forces were almost always collected on the top of the frozen droplet surface. The EB button sample is commonly used for the cleanliness evaluation of the alloys. This technique is described in detail in Appendix B.

4.5. Chemical Analysis

4.5.1. Analysis of Major Elements

Major elements of cast samples such as chromium, cobalt, molybdenum, titanium,
Figure 4.5 Two types of EB melted samples. a) A droplet sample, and b) a button sample.
aluminum, etc. were analyzed by Energy Dispersive X-ray Spectroscopy (EDX), Kevex analyst 8000, and Wavelength Dispersive X-ray Spectrometer (WDX), Microspec WDX-3PC, that are mounted on Scanning Electron Microscope (SEM) HITACHI S-570. EDX and WDX are used for both qualitative and quantitative analysis.

EDX is mainly used only for the analysis of transition elements such as Ni, Cr, Co, Ti, etc. because there are detection difficulty and a low accuracy in quantitative analysis of light elements such as C, Al due to low energies of radiated X-rays. On the other hand, WDX is utilized for the analysis of both light and transition elements. In WDX analysis, the intensity of the characteristic X-ray detected from the element to be examined were calibrated using a standard sample at the beginning of measurement.

In order to analyze quantitatively, two methods were taken: spot analysis and area analysis. Spot analysis was applied for the identification of tiny particles where the spot size varied from 1 μm to few μm, depending on accelerating voltage and current. Area analysis was applied for the analysis of average composition of relatively large particles and for qualitative analysis. Area analyzed ranged approximately from 300 μm² to 0.5 mm².

4.5.2. Analysis of Gas Element

Nitrogen and oxygen analysis was performed using the inert carrier-gas method. The equipment employed is a HORIBA EMGA-2200 analyzer at Sanyo Special Steel Co., Ltd. that consists of gas analyzer and induction furnace. In the furnace, a carbon crucible is used. Standard samples, containing 6 ppm nitrogen, and containing 3.7 ppm oxygen, were used for nitrogen and oxygen calibrations, respectively.
Chapter 4  Experimental Work

Two of approximately 1 g solid, clean samples of the alloy (5 x 5 x 5 mm) were analyzed for both nitrogen and oxygen analysis. The values from two samples were within the range of ±2 ppm for nitrogen analysis and within ±1 ppm for oxygen analysis while the precision of the equipment were indicated as ±3 ppm for nitrogen analysis and ±1 ppm for oxygen analysis.

4.5.3. Identification of MC Carbide

MC carbides contained in cast IN100 were identified by using a RIGAKU Rotating Anode X-ray diffractometer, located in the department of physics, UBC, which can analyze small samples of powder. The diffractometer is fully computer controlled and the data obtained are automatically saved. Calibration of this device is done every morning before experiments are carried out. The settings of the X-ray diffractometer used for analyzing the MC carbide powder were:

<table>
<thead>
<tr>
<th>Setting</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC carbide powder</td>
<td>approximately 30 mg</td>
</tr>
<tr>
<td>2 Theta range</td>
<td>41 – 42 degree</td>
</tr>
<tr>
<td>Scan speed of goniometer</td>
<td>0.1 degree/2 Theta/min.</td>
</tr>
<tr>
<td>Data sampling rate</td>
<td>0.02 degree/2 Theta</td>
</tr>
<tr>
<td>Acceleration voltage</td>
<td>50 KeV</td>
</tr>
<tr>
<td>Tube current</td>
<td>180 mA</td>
</tr>
<tr>
<td>Target and radiation</td>
<td>Cu, $\lambda_{K\alpha(avg)} = 1.541871$ Å</td>
</tr>
</tbody>
</table>

The powder sample for X-ray diffraction measurement was extracted electrochemically from the cast sample. Since IN100 contains a large amount of Ni$_3$(Al,Ti)
\[ \gamma', \text{ an electrolyte that can dissolve both the matrix and } \gamma' \text{ was chosen.} \] Appendix D describes the electrolytic extraction method in detail.

### 4.6. Observation of Structure

Mechanically polished surface were used for microstructural observation and prepared by using abrasive paper and diamond paste. For carbide and inclusion (oxide, nitride) observations, the as-polished surface was examined. For microstructural observations, an etched surface was used to reveal grain boundaries, \( \gamma - \gamma' \) eutectic and \( \gamma' \) precipitates. The etchant principally used was Kalling II reagent, which is composed of:

\[
\begin{align*}
\text{CuCl}_2 & \quad 10 \text{ g} \\
\text{HCl} & \quad 200 \text{ ml} \\
\text{Ethanol} & \quad 200 \text{ ml}
\end{align*}
\]
Chapter 5  Results and Discussion

5. Results and Discussion

5.1. Directionally Solidified Cast (DS) Sample

Directionally solidified cast (DS) samples were mostly used to investigate macro- and microstructures, morphologies and chemical compositions of MC carbides, inclusions such as TiN and HfO₂ and interdendritic segregation. Some parts of the samples were provided as the melting stocks for EB remelting experiments.

Two sets of DS samples of IN100 and Mar-M247 were used for the examinations. For IN100, samples of low nitrogen content (designated as LN) and of high nitrogen content (HN) were used. High nitrogen sample was made by an inoculation of ferro-chromium nitride powder. Single melt (S) and multiple remelt (M) DS samples, remelted seven times in the same alumina crucible, were used for Mar-M247.

5.1.1. IN100

5.1.1.1. Macrostructure

The macrostructure of DS IN100 samples consists of three regions: a small equiaxed grain region, a columnar grain region and a large equiaxed grain region, from the bottom of the sample. It can be considered that the change in structure results from the changes in solidification conditions. Figure 5.1 shows the macrostructure of the DS IN100 samples.

In practice, it is well known that solidification conditions, the thermal gradient (G) and the solidification rate (R), are the dominant factors for the change in grain morphologies,
Figure 5.1 Macrostructures of DS IN100 sample.
Chapter 5  Results and Discussion

i.e., structure.  Figure 5.2 [84] summarizes the relationship between the grain morphologies and the solidification parameters (in this Figure, R is designated as V).  It is shown that the product $G\cdot R$, equivalent to the cooling rate, controls the scale of the structures, and that the ratio $G/R$ predominantly determines the growth morphologies.

It is observed from the macrostructure that the solidification condition in the DS samples, are not constant but change continuously.  Figure 5.3 indicates the estimated solidification parameters of the DS sample cast for this work with the morphology transition boundaries taken from the literature [85].  The solidification data used for the estimation includes eight alloys of different DS conditions, i.e., solidification power settings [86].  Figure 5.4 shows the temperature profile change during solidification of DS samples under the induction power settings of 11 kW melting and 4 kW solidification.

It is indicated from Figure 5.3 that the solidification condition in the DS samples moves from a large $G$ and small $R$ region to a small $G$ and large $R$ region, and that the cooling rate $G\cdot R$ decreased gradually with moving the solidification front upward.  In the DS samples, the morphology changed from cellular to dendritic immediately after directional solidification started.  The grain grew in a dendritic manner and some grew larger by interrupting other grains.  Then solidification ended as a large equiaxed structure when the condition crossed the columnar equiaxed transition (CET) boundary.  Since the last liquid froze in this region, relatively large pores caused by shrinkage were observed.  The structural change in scale shows a good agreement with this change in the solidification conditions, i.e., the cooling rate $G\cdot R$.  

93
Figure 5.2 Relationship between solidification morphologies and conditions [84].

$G$: thermal gradient, $V$: solidification rate.
Figure 5.3 Range of solidification parameters of DS sample. Top and Bottom in the Figure refer to the positions of the DS samples.
Figure 5.4 Temperature changes in DS IN100 sample during directional solidification. Power settings were 11 kW for melting and 4 kW for solidification.
5.1.1.2. Chemical Composition

Analyses of nitrogen contents in DS IN100 samples were carried out at different positions, corresponding to carbide morphologies: the bottom and top parts of the columnar region. Table 5.1 lists the analyses.

In both DS samples, nitrogen contents at the bottom part were higher than at the top part. However, the contents at the top part were constant at about 10 ppm. It appears that an inoculation of nitrogen affects only the nitrogen content at the bottom part, and that nitrogen content seems to saturate to a level of about 10 ppm at the top part.

5.1.1.3. Interdendritic Segregation

Interdendritic segregation of major elements in the DS sample was analyzed using a transverse section of the columnar region. Figure 5.5 shows the variations of the elements during freezing with that of fraction solidified. Table 5.2 summarizes the segregation coefficients calculated from the analysis with those obtained from Ni-X binary phase diagram.

Among major elements, Ti segregated strongly to the liquid, i.e., interdendritic region. Cr and Al weakly segregate to the interdendritic region, and conversely, Co segregated to the solid, i.e., dendrite. Mo and V had no tendency to segregate to either the solid or the liquid. It is expected that the titanium concentration, the element of interest, increases with freezing and that it rises up to about 6 wt.% at around 1310°C, at which MC carbide will form. At this temperature, it can be estimated from the calculation of the solubility product that the nitrogen limit for TiN precipitation is lowered to 3.3 ppm.
Chapter 5  Results and Discussion

Table 5.1  Nitrogen contents in columnar region of DS IN100 samples.

<table>
<thead>
<tr>
<th>designation</th>
<th>Bottom (Blocky carbide) part</th>
<th>Top (Chinese script carbide) part</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN100 LN*</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>IN100 HN*</td>
<td>26</td>
<td>10</td>
</tr>
</tbody>
</table>

* LN: low nitrogen, HN: high nitrogen (nitrogen-inoculated) sample

** An error for each analysis was ±3 ppm.

Table 5.2  Segregation coefficients for major elements in IN100.

<table>
<thead>
<tr>
<th>Segregation coefficient</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>V</th>
<th>Al</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{calc.}$ *</td>
<td>0.99</td>
<td>1.07</td>
<td>1.00</td>
<td>1.00</td>
<td>0.99</td>
<td>0.63</td>
</tr>
<tr>
<td>$k_{binary.}$ **</td>
<td>0.93</td>
<td>1.00</td>
<td>0.67</td>
<td>0.85</td>
<td>0.80</td>
<td>0.70</td>
</tr>
</tbody>
</table>

* $k_{calc.}$ was calculated from the result of analysis.

** $k_{binary.}$ was calculated using Ni-X binary phase diagram by approximating the liquidus and solidus curves as straight lines.
Figure 5.5 The variations of major elements during solidification in IN100.
Chapter 5 Results and Discussion

5.1.1.4. Microstructure

The microstructures of IN100 and Mar-M247 alloys consist of MC carbide, fine Ni₃(Al,Ti) γ' precipitates distributed in the matrix, γ-γ' eutectic, microporosity and the γ matrix.

5.1.1.4.1. Morphology of MC Carbide

Two morphologies of MC carbides were observed in the columnar region of the DS sample: blocky carbides and Chinese script or herringbone type carbides. The former was located mostly in the lower part of a columnar region where solidification conditions were large G and small R, and the latter was found in the upper part where the parameters were conversely small G and large R. In the middle, both morphologies of carbides were observed as a transition area of carbide morphology and the location of the transition was the same in both LN and HN samples. It can then be concluded that the solidification condition not the nitrogen content determines carbide morphology The change in morphology of carbides is shown in Figure 5.6, and carbide morphology in relation to solidification conditions is shown in Figure 5.7.

The other remarkable difference associated with carbide morphology was the existence of TiN particles. TiN particles were only observed in the lower part of a columnar region, where the dominant carbide morphology is blocky, and they appeared to be cores of carbides. Some of the carbides precipitated on the oxide, Al₂O₃, and some precipitated on TiN that had formed on the oxide. Figure 5.8 shows a TiN particle that acts as the core of a blocky carbide. On the other hand, no TiN particles were found in the Chinese script carbide area by optical microscopy or SEM observations.
Figure 5.6 Carbide morphology change in DS sample of IN100. a) Top, b) middle, and c) bottom part of the columnar region. Magnification 200 times.
Figure 5.7 Carbide morphology boundaries with the solidification conditions of DS specimens.
Chapter 5  Results and Discussion

Fernandez et al. [87] investigated the relationship between carbide morphology and the solidification condition of IN100, as shown in Figure 5.9 (summarized by Tien in [88]). They suggested that the volume percent of blocky carbides increases with decreasing R or increasing G, hence with increasing G/R ratio. The volume percent of the Chinese script carbides exhibits an inverse variation. While nucleation of blocky carbides on TiN or oxide particles was not discussed in [87], the change in MC carbide morphologies found here agrees with their investigations.

5.1.1.4.2. Distribution of Titanium Nitride

The distribution of TiN particles was not uniform and they were observed in predominantly two regions: the lower part of a columnar region, at which blocky carbide formed, and the top surface of the large equiaxed region, i.e., the last region to solidify. Figure 5.10 shows TiN precipitates in both regions. No discrete TiN particles were found in Chinese script carbide area.

At the lower part of columnar region, all TiN particles were contained in MC carbides. They seem to be nucleation cores of the carbides. Figure 5.11 shows TiN particle and blocky carbide with elemental analysis. Since some TiN precipitated on Al₂O₃ oxide particles, such particles seemed to form heterogeneously on the oxides and then to act as cores for carbide precipitation. The size of TiN particles found in this region was relatively small and ranged from 2 to 8 μm on observed metallographical sections.

At the top surface of the large equiaxed region, agglomerated TiN particles surrounded by carbides were observed. They were relatively large particles ranging from 5 to 18 μm.
Figure 5.8 TiN particle that acts as a nucleating core of blocky carbide.

Figure 5.9 The volume fraction and morphology of MC carbides in DS IN100 [88].
Chapter 5  Results and Discussion

Figure 5.10  Titanium nitride precipitates in a) top surface of large equiaxed region and b) the lower area of columnar region.
Figure 5.11 TiN particle and blocky carbide with elemental analysis. a) SEM image, b) titanium and c) nitrogen distributions. Magnification: 3000 times. Darker region is TiN surrounded by carbide (light gray region).
Chapter 5  Results and Discussion

It is expected that such TiN particles precipitated during freezing, floated up due to buoyancy and convection, and agglomerated at the surface.

The uneven distribution of TiN is considered to be due to following mechanism: TiN will form during freezing when titanium and nitrogen concentrations exceed the solubility limit, i.e., solubility product of TiN. At the bottom of the columnar region where the solidification rate \( R \) is large compared to the terminal velocity of TiN, about 0.01 mm/sec (Figure 5.12), a relatively small TiN is trapped at the solidification front and becomes the nucleus of a carbide. Above this region, TiN will grow larger due to a decrease in the thermal gradient \( G \) or a stable temperature profile. With an increase the terminal velocity, about 0.1 mm/sec, due to the growth of TiN, almost all TiN will float to the liquid surface. Consequently, there is no TiN found at the top of columnar region.

5.1.1.4.3. Composition of MC Carbide

The chemical compositions of MC carbides were identified. Table 5.3 shows the results, and the stoichiometric formulae of both blocky and Chinese script carbides were obtained as:

\[
\begin{align*}
(Ti_{0.73}Mo_{0.21}V_{0.04}Cr_{0.02})C & \quad \text{Blocky type in lower part} \\
(Ti_{0.90}Mo_{0.05}V_{0.04}Cr_{0.01})C & \quad \text{Blocky type in upper part, with Chinese script type} \\
(Ti_{0.76}Mo_{0.16}V_{0.06}Cr_{0.02})C & \quad \text{Chinese script type.}
\end{align*}
\]

There were no differences in compositions between low and high nitrogen DS samples. It is obvious that the MC carbide in IN100 is composed principally of Ti and Mo with small amounts of V and Cr. Chinese script carbide is slightly richer in Ti and poorer in Mo than the blocky carbide.
Figure 5.12 Calculated terminal velocity of TiN particle in IN100.
Table 5.3 Compositions of the various types of MC carbides in IN100.

<table>
<thead>
<tr>
<th>Element</th>
<th>Blocky carbide</th>
<th>Blocky carbide found with Chinese script type</th>
<th>Chinese script type carbide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>36.3</td>
<td>44.8</td>
<td>37.9</td>
</tr>
<tr>
<td>Mo</td>
<td>10.6</td>
<td>2.5</td>
<td>7.7</td>
</tr>
<tr>
<td>V</td>
<td>2.3</td>
<td>1.8</td>
<td>2.6</td>
</tr>
<tr>
<td>Cr</td>
<td>0.9</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>49.9</td>
<td>50.4</td>
<td>50.9</td>
</tr>
</tbody>
</table>

* All the values were average of 10 carbides.

* Contents were normalized to 100.

* The values of 2 sigma was approximately 0.2 for Ti, 0.2 for Mo, 0.1 for V, 0.05 for Cr and 3.2 for C.
Chapter 5  Results and Discussion

The formulae of blocky and Chinese script type carbides have been reported in the literature [61,87] to be:

\[(\text{Ti}_{0.72}\text{Mo}_{0.17}\text{V}_{0.06}\text{Cr}_{0.02})\text{C} \quad \text{Blocky type}\]
\[(\text{Ti}_{0.76}\text{Mo}_{0.15}\text{V}_{0.06}\text{Cr}_{0.03})\text{C} \quad \text{Chinese script type.}\]

It can be concluded that both types of carbides found in the DS samples and those reported in the literature are identical.

There is no literature discussion about blocky carbides with high Ti content that are found in conjunction with Chinese script carbides. However, since these carbides contain higher fraction of Ti and lower of Mo, V and Cr than others, it is assumed from distribution of TiN that they may be carbonitrides. Formation mechanism is considered that relatively small, floating TiN were trapped, carbide precipitated on them, and then they solid-solutioned each other during freezing, when the thermal gradient was small and the temperature was kept high for a relatively long time. These carbides occupied only a small fraction, approximately 0.3 %, of all carbides in this region.

5.1.1.4.4. Microporosity

Shape, size and average fraction of area of microporosity at both blocky and Chinese script carbide parts of the columnar region were examined. The results are summarized in Table 5.4.

In the blocky carbide region, the shapes of microporosity were almost spherical or elongated along the direction of solidification in metallographical sections. Round pores were 10 – 50 μm in diameter and elongated ones were approximately 10 – 20 μm in width.
Table 5.4. Microporosity in the columnar region of DS IN100 sample.

<table>
<thead>
<tr>
<th></th>
<th>Blocky carbide part</th>
<th>Chinese script carbide part</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shape</strong></td>
<td>• spherical or elongated</td>
<td>• irregular</td>
</tr>
<tr>
<td><strong>Size</strong></td>
<td>• 10 – 50 μm in diameter</td>
<td>• 5 – 30 × 10 – 50 μm in LN sample</td>
</tr>
<tr>
<td></td>
<td>• 10 – 20 × 20 – 80 μm</td>
<td>• 5 – 30 × 15 – 80 μm in HN sample</td>
</tr>
<tr>
<td><strong>Location</strong></td>
<td>• in the dendrite</td>
<td>• at the dendrite boundary</td>
</tr>
<tr>
<td></td>
<td>• at the dendrite boundary</td>
<td>• at the dendrite boundary</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>• 0.028 % in LN sample</td>
<td>• 0.016 % in LN sample</td>
</tr>
<tr>
<td><strong>area fraction</strong></td>
<td>• 0.040 % in HN sample</td>
<td>• 0.024 % in HN sample</td>
</tr>
</tbody>
</table>
and 20 – 80 µm in length. They were observed both in the dendrite and at the dendrite boundaries. There was no evidence that the location of microporosity was related to that of blocky carbide. There were also no differences in shape and size between high nitrogen (HN) and low nitrogen (LN) samples except in average area fraction. The average area fractions were 0.028 % in LN sample and 0.040 % in HN sample.

In the Chinese script carbide region, the microporosities were located only at the dendrite boundaries and showed irregular shapes. Their sizes were 5 – 30 µm in width and 10 – 50 µm in length for those observed in the LN sample, and 5 – 30 µm in width and 15 – 80 µm in length for found in the HN sample. Unlike in the blocky carbide part, they were always found with γ-γ’ eutectics. The average area fractions of microporosity were 0.016 % in the LN sample and 0.024 % in the HN sample.

5.1.1.5. Identification of Chinese Script MC Carbide

No TiN particles were found in the Chinese script carbide region of either LN or HN samples, however, the nitrogen contents appeared to saturate near 10 ppm. Since the estimated solubility of nitrogen is 5 ppm at the liquidus, the difference of about 5 ppm in nitrogen content is expected to be present in nitride precipitates or dissolved in the alloy, either in matrix or in second phases such as carbides. The most practical assumption is that the excess nitrogen may dissolve in carbides or that TiN may diffuse into carbide under conditions where thermal gradient is small and the liquid is kept warm for a relatively long time.

Figure 5.13 shows the appearance of extracted carbides and Figure 5.14 shows X ray diffraction patterns of Chinese script carbides. Intensities of all peaks were normalized to
Figure 5.13 Appearance of extracted Chinese script MC carbide.
Figure 5.14 X-ray diffraction patterns for Chinese script type carbides extracted from DS specimen. All peaks are from $hkl = 200$. 
Chapter 5  Results and Discussion

100. As references, TiN powder and \( 2\theta \) values of both TiC and TiN cited from the literature [89] were used. The peaks taken from Chinese script carbides were located near the TiC peak between those of TiC and TiN. It is possible, therefore, that Chinese script carbide is not a carbide but a carbonitride that contains a smaller amount of nitrogen than carbon. However since the carbide contains substitutional elements other than Ti the peak shift from pure TiC must also take this into account.

Ozturk et al. [89] summarized that the strongest peak \((hkl = 200)\) of Ti(C,N) is between pure TiC and TiN and that the lattice parameter, \( a_{\text{Ti(C,N)}} \), has a linear dependence on the mole fraction of TiN. The linear dependence follows a line joining the values of TiN and TiC, i.e., 4.2350 Å and 4.3274 Å, respectively. The line is defined as the equation:

\[
a_{\text{Ti(C,N)}} (\text{Å}) = 4.3274 - 9.2 \times 10^{-4} \times (\text{mole fraction of TiN})
\]

Applying this composition dependence on lattice parameter to the result, the lattice parameter of Chinese script carbides was calculated as:

\[
a_{\text{Chinese}} = 4.3051 \text{ Å}.
\]

Wlodek [90] reported that the lattice parameter of Ti(C,N), \( a_{\text{Ti(C,N)}} \), in IN100 was 4.31 Å. The obtained value shows agreement with his result. It is therefore calculated that Chinese script carbides contain about 6 wt.% of nitrogen, and assuming that all nitrogen is solutioned in the carbides, it follows that bulk IN100 contains 500 ppm of nitrogen based on the weight of extracted Chinese script carbides, 0.0954 g from 11.23 g of bulk IN100. However, the nitrogen content analyzed by the inert carrier-gas method was 10 ppm, which is equivalent to 0.12 wt.% of nitrogen content in the carbides. The possible reason for such a large discrepancy in nitrogen content calculated from the lattice parameter is that Mo, Cr and V dissolved in the carbide would shift the peaks to the TiN side, i.e., the lattice parameter of the Chinese script carbide would be increased.
Chapter 5  Results and Discussion

5.1.2. Mar-M247

5.1.2.1. Macrostructure

The macrostructure of the DS Mar-M247 samples were almost the same as that of DS IN100, consisting of fine equiaxed, columnar, and large equiaxed regions. Figure 5.15 shows the macrostructures of the DS Mar-M 247 samples. The difference between two Mar-M247 at DS IN100 was the length of the columnar region, which is due to the difference in directional solidification conditions, i.e., power settings. Power settings for Mar-M247 were 9 kW for melting and 2 kW for solidification.

5.1.2.2. Chemical Composition

Oxygen contents in both single melted (S) and multiple remelted (M) samples were analyzed. Table 5.5 shows the result. Samples for oxygen analysis were taken from the bottom and top part of the columnar region.

It is obvious that oxygen contents in the multiple remelt sample were almost doubled compared to those in the single melt sample. The reason for the increased oxygen level is considered due to the reaction of hafnium with the alumina crucible during remelting expressed by the equation:

\[ 3\text{Hf} + 2\text{Al}_2\text{O}_3 (s) = 4\text{Al} + 3\text{HfO}_2 (s) \]  

(3.42)

5.1.2.3. Interdendritic Segregation
Figure 5.15 Macrostructures of DS Mar-M247 samples.

Table 5.5 Oxygen contents in columnar region of DS Mar-M247 samples.

<table>
<thead>
<tr>
<th>designation</th>
<th>Bottom part</th>
<th>Top part</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mar-M247 S*</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Mar-M247 M*</td>
<td>7</td>
<td>6</td>
</tr>
</tbody>
</table>

* S: single melt, M: multiple remelt sample

** An error for each analysis was ± 1 ppm.
The variations in concentration of the major elements with fraction solidified during solidification, due to interdendritic segregation were shown in Figure 5.16, for Mar-M002 [46]. Segregation coefficients calculated from the analyses are listed in Table 5.6.

In DS Mar-M247, tantalum, aluminum and titanium were found to segregate to the liquid, i.e., interdendritic region, and hafnium has a strong tendency to segregate to the liquid. Cobalt and tungsten segregated to the solid, and chromium and molybdenum did not segregate consistently to either the liquid or solid.

Zeisler-Mashi et al. [91] investigated the segregation phenomena during solidification of Mar-M247. Segregation coefficients they obtained are listed in Table 5.6. This reported tendency for segregation of each element agrees with the present results. It is inferred that the difference in values of the coefficients was due to the diffusion of elements in solid caused by relatively fast cooling rate of their samples.

5.1.2.4. Microstructure

5.1.2.4.1. Morphology of MC Carbide

Morphologies of MC carbide observed in the columnar region of DS Mar-M247 samples were the same as in IN100: blocky type and Chinese script type carbides. However, they seemed to be insensitive to the change in morphologies due to solidification condition because the morphology did not change significantly between the bottom and the top part. There was no difference in morphologies between single melted (S) and multiple remelt (M) sample. Figure 5.17 shows the carbide morphology in different part of Mar-M247.
Figure 5.16 The variations of major elements during solidification in Mar-M247.

Table 5.6 Segregation coefficients for major elements in Mar-M247.

<table>
<thead>
<tr>
<th>Segregation coefficient</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>Al</th>
<th>Ti</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{calc}}$ *</td>
<td>1.00</td>
<td>1.07</td>
<td>1.00</td>
<td>1.18</td>
<td>0.79</td>
<td>0.97</td>
<td>0.76</td>
<td>0.13</td>
</tr>
<tr>
<td>$k_{\text{ref}}$ **</td>
<td>1.00</td>
<td>1.07</td>
<td>1.00</td>
<td>1.23</td>
<td>0.77</td>
<td>0.94</td>
<td>0.73</td>
<td>0.12</td>
</tr>
<tr>
<td>$k_{\text{binary}}$ ***</td>
<td>0.93</td>
<td>1.00</td>
<td>0.67</td>
<td>1.40</td>
<td>0.82</td>
<td>0.80</td>
<td>0.70</td>
<td>0.10</td>
</tr>
</tbody>
</table>

* $k_{\text{calc}}$ was calculated from the result of analysis.
** $k_{\text{ref}}$ was taken from the literature [91].
*** $k_{\text{binary}}$ was calculated using Ni-X binary phase diagram by approximating the liquidus and solidus curves as straight lines.
Figure 5.17 Morphology of MC carbides in DS Mar-M247 sample. a) Top, b) middle and c) bottom part of the columnar region. Magnification 200 times.
5.1.2.4.2. Composition of MC Carbide

In both S and M samples, compositions of MC carbides, either blocky or Chinese script type, appeared to be identical. The stoichiometry of the MC carbide was approximately:

$$(Ta_{0.42}Ti_{0.25}Hf_{0.16}W_{0.12}Cr_{0.01})C.$$ 

During analysis, a large fluctuation in Hf concentration was observed, ranging from 0.06 to 0.45 at. %. This appeared to be affected apparently the concentrations of other elements because the analysis program used with EDX and WDX forced the sum of the concentrations to be 100 at. %.

Such a fluctuation in Hf concentration seems to be due to the nonuniformity of Hf distribution in the MC carbide. Dahl et al. [92] suggested that there was a region in MC carbide of Hf-modified, at which Hf concentration was highest and Ti and W contents were reduced by replace of both of these elements. Yunrong et al. [93] explained this phenomenon by conjugation of two types of MC carbide, Ti-rich and Hf-rich carbides. They suggested from their investigations that Ta-rich carbide existed at the center and a Hf-rich carbide was present at the edge of MC carbide. Figure 5.18 shows elemental line traces for the elements of Hf-modified Mar-M246 [92].

5.1.2.4.3. Hafnium Oxide

No HfO$_2$ particles was observed clearly in the metallographical sections of both DS samples. Only Al$_2$O$_3$ particles were found. It is believed that either the size of HfO$_2$ particles are too small to be detected by microscopic observation or because only a small
Figure 5.18 Elemental line trace for five elements in Mar-M246-Hf. Electron beam scanned along a line designated by the arrows. Magnification 3000 times.

[92]
umber of HfO$_2$ particles exist in the DS samples. However, it is expected that HfO$_2$ may be distributed uniformly throughout the columnar region, even though it is not observed distinctly because HfO$_2$ which may form during remelting due to the reaction with the alumina crucible will be well mixed by convection of the liquid.

5.1.3. Effects of TiN and Solidification Condition on DS IN100 Sample

It was found that TiN precipitated during freezing when the nitrogen concentration exceeded the saturation solubility of TiN, as determined from the solubility product. Small TiN particles were trapped by the solidification front when the solidification rate was larger than the terminal velocity of TiN and became the nuclei for carbide growth. Relatively large TiN particles grew by a diffusion mechanism and escaped to the top surface of the liquid, due to the fact that they had a larger terminal velocity than the solidification rate.

While MC carbide morphology and the microporosity level are related to the nitrogen content, i.e., existence of TiN, it is suggested that the predominant factor for the change in carbide morphology is the solidification conditions, $G$ and $R$ (hence, $G/R$). This can be concluded from the fact that the relative positions of the carbide morphology transition area are the same in both LN and HN DS samples. As a result, it can be suggested that the solidification condition, $G/R$, determines the carbide morphology and that nitrogen content in the liquid only affects the total number of TiN particles. Whether TiN is trapped or floats is determined by the terminal velocity (size of TiN particle) relative to the solidification rate of the casting.

The microporosity level is mainly controlled by the carbide morphology, which is associated with the solidification condition. There is a relation between the blocky carbide
and microporosity. Blocky carbide would promote the formation of microporosity by the blockage of liquid flow into the interdendritic path. TiN particles contribute to this mechanism as shown in Table 5.4.

5.2. EB Melted Sample

Two types of EB remelted sample were used for examination: a droplet sample melted from a DS sample and a button sample from the master ingot. The constitutions of the raft area were analyzed by EDX or WDX. Figure 5.19 shows an example of the appearance of the raft of EB melted samples.

5.2.1. IN100

The raft on both droplet and button samples of IN100 mostly consisted of Al₂O₃ particles and faceted MC carbides. There was no remarkable difference in the normalized raft area of both droplet samples. However, the raft of the button sample occupied a large normalized area compared to droplet samples. This is because almost all area of the raft was occupied by Al₂O₃ particles and because the master ingot was considered to contain large amount of oxides, mostly Al₂O₃, in the centre pores. A summary of the normalized raft area is shown in Table 5.7.

It was difficult to find single TiN particle in the raft area. Almost all TiN particles were enclosed by faceted MC carbides. It is assumed that TiN particles are retained on the liquid surface due to interfacial tension forces between TiN and liquid during remelting and that MC carbides re-precipitate during freezing on TiN particles that are floating on the
Figure 5.19 Appearance of the raft of EB remelted sample. Photograph was taken from droplet sample of IN100. Magnification 10 times.
liquid-free surface. The fact that the carbides were faceted demonstrates that they were formed during the freezing of the liquid and were not carbides retained from the original melting stock, since Chinese script morphology is characteristic of the high freezing rate of the EB button surface.

During observation by optical and SEM microscopy, no TiN particles were found in the top (beneath the raft area) of the button sample, where the morphology of MC carbide was Chinese script type (Figure 5.20) and for which the nitrogen content was ranging from 5 to 6 ppm. The reduction in nitrogen content is considered mainly due to separation of TiN particles to the raft. This value (5 - 6 ppm) is probably slightly higher than the saturation solubility of TiN at the liquidus temperature.

It is assumed that particles such as TiN and Al₂O₃ found on the raft surface are principally collected by the interfacial tension force between the particles and the liquid, not by gravitational flotation. This is expected from the fact that the droplet samples, in which solidification is so fast, form the raft on the top surface and that floating raft can be observed immediately after the alloy stock becomes molten in the copper crucible. Therefore, it can be considered that inclusion particles will be retained on the surface of the liquid droplet that is formed on the melt stock. Even after the liquid droplet falls onto the melt pool, the interfacial tension force will hold those inclusions on the free liquid surface.

5.2.2. Mar-M247

The raft of EB remelted samples of Mar-M247 contains oxides of Al₂O₃ and HfO₂ and carbides. HfO₂ particles found on the raft were distinguishable from Al₂O₃ particle due to their flaky shapes compared to the round shapes of Al₂O₃. The compositions of HfO₂
Table 5.7 Summary of the normalized raft area of EB remelted IN100.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Normalized raft area (cm²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Droplet</td>
<td></td>
</tr>
<tr>
<td>DS, low nitrogen (LN)</td>
<td>15.1</td>
</tr>
<tr>
<td>DS, high nitrogen (HN)</td>
<td>16.8</td>
</tr>
<tr>
<td>Button</td>
<td></td>
</tr>
<tr>
<td>Master ingot</td>
<td>41.6</td>
</tr>
</tbody>
</table>

Figure 5.20 Microstructure of EB remelted button sample of IN100. Photograph was taken from top of the button sample. (Magnification: 400 times)
particles appeared to be almost pure HfO₂, not a complex Al-Hf-O type oxide. Figure 5.21 shows a HfO₂ particle found in the raft, together with an elemental distribution map.

The normalized raft areas of EB remelted samples are listed in Table 5.8. The results seemed to be dependent on the oxygen content of the starting materials for EB remelting, and therefore the droplet remelted from the multiple remelt DS sample showed the largest normalized area. Oxygen contents of the button sample were between 1 and 3 ppm with an analysis error of ± 1 ppm. It was expected to improve oxide cleanliness due to the separation of HfO₂ to the raft, though there was no clear difference in oxygen content between master ingot and remelted button sample.

It is considered that separation of HfO₂ particles was carried out by the same mechanism as the case of TiN in IN100, i.e., interfacial tension force. Assuming the density difference relative to that of the melt is a dominant factor of separation, HfO₂, which has higher density of 10 g/cm³, should sink to the bottom in the liquid pool. From the fact that HfO₂ is collected on the raft area of the droplet and button samples, it is considered the interfacial tension forces retain HfO₂ particles (and other inclusions) pre-existing in the melt stock onto the liquid free surface.

5.3. Removal of TiN and HfO₂ by EB remelting

From this work, it was clearly indicated that the dominant separation mechanism of pre-existing inclusions in melt stocks (such as TiN and HfO₂) during a remelting process was not due to the relative density difference between the particles and the melt, i.e., flotation or sinking, but due to the interfacial tension forces between the particles and the liquid surface. TiN particles formed during a slow freezing process can float to a liquid free surface.
Hafnium oxide found on the raft of EB melted sample with elemental analysis by WDX. Magnification 3000 times.
Chapter 5  Results and Discussion

Table 5.8 Summary of the normalized raft area of EB remelted Mar-M247.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Normalized raft area (cm²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Droplet DS, single melt (S)</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>DS, multiple remelt (M)</td>
</tr>
<tr>
<td>Button Master ingot</td>
<td></td>
</tr>
</tbody>
</table>
In practical EBCHR processes, the cold hearth has been designed based on the idea that the refining will carried out mostly by relative density difference. For example, an inclusion barrier, whether mechanical or thermal, is located at the pouring end of the hearth. It is however obvious that TiN or HfO₂ can be separated at the first stage of remelting on the liquid free surface. This suggests that for the most effective separation, the inclusion barrier should be located at the remelting stage, i.e., immediately after the molten droplet from the melt stock falls on to the liquid pool.

The long residence time of the liquid on the hearth can be made use for another purpose: removal of nitrogen directly from the melt. In the usual case, EBCHR will be operated at a high vacuum level of 10⁻⁵ to 10⁻⁶ torr. Such a high vacuum level will remove nitrogen from the melt, following Sieverts' Law, while the melt resides on the hearth. During this stage, the temperature of the melt must be kept as low as possible near the liquidus temperature of the alloy because the solubility of nitrogen of all nickel base alloys increases with increasing the melt temperature. The lower temperature may also prevent the evaporation loss of certain elements such as chromium.

Figure 22 shows an example of the temperature profile in the pool [94] in the case of titanium. While the profile depends on thermal conductivity of copper hearth, liquid volume or weight and melting rate, the maximum depth of the pool is approximately 20 mm and the temperature difference between top and the bottom of the pool is roughly 100 °C. It is therefore expected that the pool temperature should be kept at around 1430 °C in the case of IN100 or, in other words, it should be controlled at $T_{\text{liquidus}} + 100 °C$. 

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Figure 5.22 Temperature profile in the cold hearth of EBCHR process. [94]
Chapter 6  Conclusions

6. Conclusions

The following itemized conclusions may be drawn from the results of this investigation:

6.1. TiN in IN100

- The solubility of nitrogen, which depends the nitrogen partial pressure and the melt temperature, was calculated to be approximately 3 ppm at the partial pressure of $10^3$ torr at the liquidus temperature of IN100.

- The solubility product of TiN in IN100 at the liquidus temperature was calculated as $\log K'_{\text{TiN}} = -2.62$, which was equivalent to about 5 ppm nitrogen at 4.7 wt.% titanium.

- The titanium concentration rose to about 6 wt.% at 1310 °C due to the segregation at which MC carbide precipitated. At this temperature, it was calculated that the nitrogen limit for TiN precipitation was lowered to about 3.3 ppm.

- It was observed that changes in MC carbide morphology were controlled by the change in solidification conditions, even though the blocky carbides are nucleated by TiN.

- In DS samples, small TiN particles were trapped by the solidification front where the solidification rate is large compared to the terminal velocity of floating TiN. Such TiN particles acted as nuclei for blocky type carbide precipitation.
Chapter 6  Conclusions

- Relatively large TiN particles grew by a diffusion mechanism and could float up to the liquid surface when the solidification rate was smaller than their terminal velocity and when TiN could reside for a long enough time to float. Some of the floating TiN could be captured toward the limit of the columnar region, and the faceted carbonitride would form in the Chinese script carbides region.

- In the Chinese script carbide region, total nitrogen content saturated at about 10 ppm. This nitrogen might be dissolved in the Chinese script carbide, where the nitrogen content was calculated to be about 0.12 wt.%.

- The solidification condition, e.g., $G/R$, associated with TiN flotation, determined MC carbide morphology. Nitrogen content of the alloy affected the number of TiN particles rather than the carbide morphology.

- The level of microporosity was dependent on nitrogen content, and its formation mechanism was probably due to the blockage of the interdendritic flow by blocky carbides.

- Pre-existing TiN particles in the EB melt stock were separated to the raft due to the retention by the interfacial tension forces rather than flotation. EB remelted button samples contained about 6 ppm nitrogen, which is probably slightly higher than the saturation solubility of TiN at the liquidus temperature.
Chapter 6  Conclusions

6.2. HfO<sub>2</sub> in Mar-M247

- It was estimated that saturation solubility of oxygen for HfO<sub>2</sub> would be less than 1 ppm at the liquidus temperature of Mar-M247. It was expected that essentially all the oxygen content in the liquid would be present as oxide particles, either Al<sub>2</sub>O<sub>3</sub> or HfO<sub>2</sub>.

- HfO<sub>2</sub> inclusions in Mar-M247 are probably formed by the reaction with the oxide crucible during melting or remelting. This implies that HfO<sub>2</sub> may also form during directional solidification process, during which the melt contacts with the oxide shell mold for a relatively long time at high temperature.

- HfO<sub>2</sub> inclusions pre-existing in the EB melt stock during remelting were separated to the raft by the interfacial tension forces between the particles and the liquid free surface. Consequently, it is concluded that the HfO<sub>2</sub> density (considerably larger than that of the melt) exhibited no influence on the separation by flotation.

Based on the experimental results, the following suggestions can be reached for practical operations.

- Under the freezing conditions necessary for DS casting, the formation of blocky carbide is inevitable. We must reduce the nitrogen content to a value below the saturation solubility of TiN at the liquidus temperature in order to avoid the additional microporosity due to TiN particles. The most practical way to achieve this objective in scrap recycling is by EBCHR with an ambient pressure of less than 10<sup>-3</sup> torr.
Chapter 6 Conclusions

- TiN, HfO₂ and Al₂O₃ particles existing in the scrap alloys can be removed effectively from the alloys using EBCHR by a process which relies on surface driven forces.

- The inclusion barrier, whether it is thermal or mechanical, must be located at the commencement of the hearth of the EBCHR process.

- The pool temperature should be kept as low as possible to avoid nitrogen dissolution into the melt over the nitrogen limit for TiN precipitation. For example, the temperature of IN100 melt should be controlled at around liquidus temperature + superheat of 100 °C, i.e., 1430 °C.

- The partial pressure of nitrogen during EBCHR operation of IN100 should be kept lower than 10⁻⁴ torr at around 1430 °C.

- A slower melting rate might be required in order to allow the dissolved nitrogen to be reduced to the equilibrium level.
Chapter 7  Suggestions for Future Work

7. Suggestions for Future Work

This work suggests further development or refinement in the following manners:

7.1. The question of nitrogen solubility in the carbides in both alloys remains unresolved. It would be of interest to determine this nitrogen content either by using analytical electron microscopy techniques or bulk chemical extraction followed by analysis.

7.2. The rate of removal of nitrogen from IN100 at nitrogen levels below the saturation solubility of TiN has been shown to be a key factor in the practical recycling of the alloy. This rate should be determined.

7.3. HfO₂ and Al₂O₃ are removed by surface driven forces. It would be of interest to determine if this process also applies to other oxide inclusions.

7.4. A system which precipitates HfN should exhibit quite different nitride particle behaviour from the TiN system studied. The proposed mechanism involving particle flotation could be verified by this means.
References

[21]: C. E. Shamblen, ibid., pp. 160.
[22]: R.C. McAllister and D. Bierstine, ibid., pp. 185.
References

[23]: R.N. Jarrett, ibid., pp. 199.
References

[50]: J. Lecomte-Bechers and M. Lamberigts, ibid., pp. 745.
[59]: T.S. Piwonka et al., Trans. AIME, 236, 1966, pp. 1157.
References

[67]: Y. Bienvenu, private communication.
[77]: F. Ishii and S. Ban-ya, Tetsu-to Hagane, 75, 12, 1989, pp. 2188.
References


Appendices
Appendices

Appendix A

Chemical Compositions of Superalloys

Appendix A will summarize chemical compositions of superalloys quoted in this thesis. The compositions listed below are nominal compositions of the alloys.

Table A  Nominal compositions of superalloys.  (wt.%)  

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<tr>
<th></th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>Nb</th>
<th>Al</th>
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<th>C</th>
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<td></td>
</tr>
<tr>
<td>AF115</td>
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<td>0.015</td>
<td>0.05</td>
<td>0.8 Hf</td>
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Appendices

Appendix B

EB Button Technique: Cleanliness Evaluation Method of Superalloys

The EB button remelt cleanliness test for nickel base superalloys was first developed by E.E. Brown in the late 1970s and has been commonly used for the cleanliness evaluation. The test method has been standardized in American Standard Test of Materials (ASTM).

The test is done by remelting the sample to be evaluated using drip melting method in the electron beam furnace[23-26]. The electron beam hits the sample and the molten droplet that may contain inclusion particles is formed. Molten droplet falls into the water-cooled copper mold and forms molten pool in which temperature is controlled by the electron beam. The beam moving a circular path on the pool surface allows the inclusion particles to float up and to gather to the center. When a certain amount of the specimen is consumed, the beam power is decreased and solidification starts. At last, finally solidified area, the center of the pool, collects the inclusion particles, which is called inclusion or particle raft area. After the pool is completely solidified and cooled, the EB button is provided to the analysis such as SEM observation and quantitative and qualitative analysis by EDX and WDX. Typical procedure of this method is illustrates in Figure B [23]

The advantages of this method are:

1) Easy operation and less time consuming compared to other method such as the electrolytic dissolution plus acid digestion method.

2) Flexibility of the sample configurations: the almost all shapes such as bars, cast blades, and cast wheels and conditions such as wrought and as cast, can be applied.
Appendices

3) Ability to make contamination from the reaction with atmosphere minimum due to high vacuum level during operation, in usual case, less than $10^{-4}$ torr.

4) Cleanliness can be compared readily between other evaluation data in terms of the normalized oxide raft area (NORA), the raft area occupied by oxide (and other inclusions) per unit weight (cm$^2$/kg).

However, there is the disadvantage which is that agglomerated inclusions can not be discovered. The agglomerated inclusions will usually act as larger inclusions than each inclusion of small size does. In this method, the agglomerated inclusions are taken apart during remelting and they are observed as a crowd of single inclusion in the raft area.
Figure B  Five-step procedure for conducting the EB button cleanliness evaluation test at Special Metals Corporation [23].
Interfacial Tension Force

The liquid has a tendency to maintain its surface area as small as possible and tries to take spherical shape under no external interaction forces. The reason of such a tendency is based on the inter molecular, tension forces at the surface, i.e., surface tension forces. Surface tension force can be interpreted as the surface free energy stored in unit surface area.

Interfacial tension forces in this work can be defined as the tension forces interacting between the particles retained on the liquid surface and the liquid metal.

In the simple case of floatation of a particle on the melt, the total upward pull force of the liquid meniscus must balance the apparent weight of the particle. Figure C.1 shows floatation of particles of different shapes. Assuming that the liquid is water, for a particle of the shape shown in Figure C.1 a), the vertical force is expressed as:

\[(\gamma_{AW}\cos\theta) \times \text{perimeter},\]

whereas for the particle in Figure C.1 b), it becomes:

\[\left\{\gamma_{AW}\cos(\theta + \theta_p)\right\} \times \text{perimeter},\]

where \(\gamma_{AW}\) is the force between atmosphere and water and \(\theta_p\) is the angle the appropriate face of the particle makes with the vertical. It has been suggested that the angle \(\theta\) is usually greater than 50° – 75° for most inclusion particles.
Figure C.1  a) Floatation of a particle by the pull of the meniscus on vertical sides, b) the floatation of a particle whose face makes an angle $\theta_p$ with the vertical.
Appendices

Appendix D

Electrolytic Extraction of MC Carbide

Electrolytic extraction method carried out in this work is to separate MC carbide particles from the cast samples. MC carbide particles extracted were used for X-ray diffraction measurement to determine whether they are carbides or carbonitrides.

The equipment used for the extraction were a stabilized DC power supply, a coulomb meter, a liquid container and an electrode as illustrated in Figure D.1. The extraction was taken place under the following conditions [56]:

- **Electrolyte**: 10% Hydrochloric acid - 1% tartaric acid - Methanol solution.
- **Current density**: 50 ~ 100 mA/cm².
- **Cathode**: Pure titanium plate, surface area is about 25 cm².

The electrolyte and current density chosen are commonly used for the electrolytic extraction of MC carbides from nickel base superalloys. The advantage of this electrolyte is that it can dissolve not only the matrix but also other second phases such as Ni₃(Al,Ti), γ', and σ phase, and that only carbides remain in the solution. This prevents the carbide residue from contamination of other phases.

After the certain amount of the sample was dissolved into the electrolyte, the electrolyte was filtrated to separate the residue, i.e., MC carbide particles, using an evacuator and a paper filter of 1 µm size as shown in Figure D.2.
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Figure D.1 Schematic configuration of electrolytic extraction cell.

Figure D.2 Filtration of the residue.